

# Liquid crystal device

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(57) Abstract: The invention relates to a device comprising at least one substrate, an electrode structure and a liquid crystalline polymer film obtainable from a polymerisable LC medium comprising one or more multi-or direactive or monoreactive mesogenic compounds, characterized in that the surface shape of said polymer film can be electrically switched. Furthermore, the invention relates to a process of production of said device, to the use of said device in an electro-opticalor electro-mechanical device and to an electro-opticalor electro-mechanical device comprising said device.



- 1 -

# **Liquid Crystal Device**

#### TECHNICAL FIELD

The invention relates to a device comprising at least one substrate
provided with an electrode structure and a liquid crystalline polymer film
obtainable from a polymerisable LC medium comprising one or more
multi-, di-, or monoreactive mesogenic compounds, characterized in that
the surface shape of said polymer film can be electrically switched.

Furthermore, the invention relates to a process of production of said
device, to the use of said device in an electro-optical or electro mechanical
device and to an electro-optical or electro-mechanical device, comprising

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# STATE OF THE ART

said device.

Surfaces are the interface between man and material and man and device. They determine the way objects feel, smooth or rough, or the way objects look, glossy or mat. In that way, they provide information by addressing senses like touch and vision. It is reported that a person can notify changes in topographical dimensions down to nanometer level [L. Skedung, M.Arvidsson, J. Young Chung, C. M. Stafford, B. Berglund, M. W. Rutland, Sci. Rep. 3, 2617 (2013)].

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Static surface topographies generated by patterned exposure to light have been studied for the fabrication of optical devices such as gratings and lenses. The principle is based on localized transport of polymeric species over micrometer dimensions, e.g. induced by continuous isomerization of incorporated azobenzene [Yager, K.; Barrett, C. "All-Optical Patterning of Azo Polymer Films" *Current Opinion in Solid State and Materials Science*, **2002**, 7].

Similarly, azobenzene derivatives were used to induce changes in shape or to transport macroscopic species over longer distances [T.M.J. White, D.J. Broer. Nature Materials 14, 1087–1098 (2015)].

Besides the activation by light, electrical fields have been used to initiate geometrical changes into polymer materials, for example, changes of their shape upon application of a voltage. Piezoelectric films are capable to deform and are used for the fabrication of microphones and loudspeakers

[E. Fukada. T. Furukawa, Ultrasonics 19 (1), 31-39 (1981)].

Electrostatic attraction between electrodes separated by an elastomeric polymer changes the shape of so-called electroactive polymers (EAPs) and may, by design, make them to perform complex mechanical functions [G. Kofod, P Sommer-larsen, R. Kornbluh and R. Pelrine, Journal of Intelligent Material Systems and Structures, 14, 787 (2003)].

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Hydrogels based on polymer, water and mobile ions deform under the action of electrical field induced ion transport causing local swelling/deswelling [Brigitte Pépin-Donat,Annie Viallat, Jean-François Blachot, and Christian Lombard, Advanced Materials 18, 1401–1405 (2006)].

For electrically triggered deformation of free-standing films there are therefore many options. It is more complicated when these films are firmly adhering to their substrates and have a rigidity that does not permit a lateral displacement of material.

Previously it has been demonstrated that additional volume is created when a polymer network with a well-ordered molecular organization is subjected to an oscillatory molecular stress [D. Liu, D. J. Broer, Nat. Commun. 6, 8334 (2015)]. Hereto films of liquid crystal polymer networks (LCNs) were used that were made by in-situ polymerization of reactive

- 3 -

mesogens. The LCNs were modified with copolymerized azobenzene crosslinks, which, by exposure to multiple wavelength light, were brought into a high frequency conformation modulation. At appropriate frequencies, the stress exerted on the polymer main chains induces resonance-enhanced oscillatory dynamics. The molecular rods of the LCN are becoming disordered while being continuously in motion. This creates dynamic mesoscopic voids. The density reduction under lateral restriction forces the films to expand in the z-direction. The topographies that are formed by a localized free volume generation have been reported to be reversible. As soon as the light is switched off they disappear and the surface changes back to its initial flat state.

However, there is a great demand with respect to devices exhibiting a dynamic surface topography which should be generated by applying an electrical field rather than by the use of light.

Surprisingly the inventors found out that this demand can be fulfilled by a device comprising at least one substrate provided with an electrode structure and a liquid crystalline polymer film obtainable from a polymerisable LC medium comprising one or more multireactive, direactive, or monoreactive mesogenic compound, characterized in that the surface shape of said polymer film can be electrically switched.

# **TERMS AND DEFINITIONS**

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The following meanings apply above and below:

The term "liquid crystal", "mesomorphic compound", or "mesogenic compound" (also shortly referred to as "mesogen") means a compound that under suitable conditions of temperature, pressure and concentration can exist as a mesophase (nematic, smectic, etc.) or in particular as a LC phase. Non-amphiphilic mesogenic compounds comprise for example one or more calamitic, banana-shaped or discotic mesogenic groups.

- 4 -

The term "mesogenic group" means a group with the ability to induce liquid-crystalline phase (or mesophase) behavior. The compounds comprising mesogenic groups do not necessarily have to exhibit a liquid-crystalline mesophase themselves. It is also possible that they show liquid-crystalline mesophases only in mixtures with other compounds, or when the mesogenic compounds or materials, or the mixtures thereof, are polymerised. This includes low-molecular-weight non-reactive liquid-crystalline compounds, reactive or polymerisable liquid-crystalline compounds, and liquid-crystalline oligomers as well as polymers. For the sake of simplicity, the term "liquid crystal" is used hereinafter for both mesogenic and LC materials.

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A calamitic mesogenic group is usually comprising a mesogenic core consisting of one or more aromatic or non-aromatic cyclic groups connected to each other directly or via linkage groups, optionally comprising terminal groups attached to the ends of the mesogenic core, and optionally comprising one or more lateral groups attached to the long side of the mesogenic core, wherein these terminal and lateral groups are usually selected e.g. from carbyl or hydrocarbyl groups, polar groups like halogen, nitro, hydroxy, etc., or polymerisable groups.

The term "reactive mesogen" means a polymerisable mesogenic or liquid crystal compound, preferably a monomeric compound. These compounds can be used as pure compounds or as mixtures of reactive mesogens with other compounds functioning as photoinitiators, inhibitors, surfactants, stabilizers, chain transfer agents, non-polymerisable compounds, isotropic monomers, etc.

Polymerisable compounds with one polymerisable group are also referred to as "monoreactive" compounds, compounds with two polymerisable groups as "direactive" compounds, and compounds with more than two polymerisable groups, i.e. three, four, five or more as "multireactive"

- 5 -

compounds. Compounds without a polymerisable group are also referred to as "non-reactive or non-polymerisable "compounds.

The terms, LC material, LC medium or LC formulation, each non-polymerisable or polymerisable or mixtures thereof, mean a material, which comprises of more than 80% by weight, preferably more than 90% by weight, more preferably more than 95% by weight of (polymerisable) LC compounds, as described above and below.

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The term "non-mesogenic compound or material" means a compound or material that does not contain a mesogenic group as defined above.

As used herein, the term "polymer" will be understood to mean a molecule that encompasses a backbone of one or more distinct types of repeating units (the smallest constitutional unit of the molecule) and is inclusive of the commonly known terms "oligomer", "copolymer", "homopolymer" and the like. Further, it will be understood that the term polymer is inclusive of, in addition to the polymer itself, residues from initiators, catalysts, and other elements attendant to the synthesis of such a polymer, where such residues are understood as not being covalently incorporated thereto.

Further, such residues and other elements, while normally removed during post polymerisation purification processes, are typically mixed or comingled with the polymer such that they generally remain with the polymer when it is transferred between vessels or between solvents or dispersion

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media.

The term "(meth)acrylic polymer" as used in the present invention includes a polymer obtained from (meth)acrylic monomers, a polymer obtainable from (meth)acrylic monomers, and a corresponding co-polymer obtainable from mixtures of such monomers.

The term "polymerisation" means the chemical process to form a polymer by bonding together multiple polymerisable groups or polymer precursors (polymerisable compounds) containing such polymerisable groups.

A "polymer network" is a network in which the linear polymer chains are additionally interconnected to form a macroscopic entity by a significant amount of crosslinks.

The polymer network can occur in the following types:

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- A graft polymer molecule, which is a branched polymer molecule in which one or more the side chains are different, structurally or configurationally, from the main chain.
- A star polymer molecule, which is a branched polymer molecule in which a single branch point gives rise to multiple linear chains or arms.

  If the arms are identical, the star polymer molecule is said to be regular. If adjacent arms are composed of different repeating subunits, the star polymer molecule is said to be variegated.
  - A comb polymer molecule, which consists of a main chain with two or more three-way branch points and linear side chains. If the arms are identical the comb polymer molecule is said to be regular.
  - A brush polymer molecule, which consists of a main chain with linear, unbranched side chains and where one or more of the branch points has four-way functionality or larger.

The terms "film" and "layer" include rigid or flexible, self-supporting or freestanding films with mechanical stability, as well as coatings or layers on a supporting substrate or between two substrates.

The term "alignment" or "orientation" relates to alignment (orientational ordering) of anisotropic units of material such as small molecules or fragments of big molecules averaged in a common direction named "alignment direction". In an aligned layer of liquid-crystalline or RM material

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the liquid-crystalline director coincides with the alignment direction so that the alignment direction corresponds to the direction of the anisotropy of the material.

The terms "uniform orientation" or "uniform alignment" of an liquidcrystalline or RM material, for example in a layer of the material, mean that the long molecular axes (in case of calamitic compounds) or the short molecular axes (in case of discotic compounds) of the liquid-crystalline or RM molecules are oriented substantially in the same direction. In other words, the lines of liquid-crystalline director are parallel.

The term "homeotropic structure" or "homeotropic orientation" refers to a film wherein the optical axis is substantially perpendicular to the plane of the film.

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

The term "tilted structure"or "tilted orientation" refers to a film wherein the optical axis is tilted at an angle  $\theta$  between 0 and 90° relative to the plane of the film.

The definitions as given in C. Tschierske, G. Pelzl and S. Diele, Angew. Chem. 2004, 116, 6340-6368 shall apply to terms related to liquid crystal materials in the instant application, which are not explicitly defined here.

For the present invention,

$$\longrightarrow$$
 ,  $\longrightarrow$  and  $\longrightarrow$  H

denote 1,4-cyclohexylene, preferably,

- 8 -

denote trans-1,4-cyclohexylene, and

denote 1,4-phenylene.

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For the present invention the groups -COO- -C(=O)O- or -CO<sub>2</sub>- denote an

or -OOC- also denote an ester group but of formula

Above and below, "carbyl group" denotes a mono- or polyvalent organic group containing at least one carbon atom which either contains no further atoms (such as, for example,  $C\equiv C$ ) or optionally contains one or more further atoms, such as, for example, N, O, S, P, Si, Se, As, Te or Ge (for example carbonyl, etc.). "Hydrocarbyl group" denotes a carbyl group, which additionally contains one or more H atoms and optionally one or more heteroatoms, such as, for example, N, O, S, P, Si, Se, As, Te or Ge.

A carbyl or hydrocarbyl group can be a saturated or unsaturated group. Unsaturated groups are, for example, aryl, alkenyl, or alkinyl groups. A carbyl or hydrocarbyl group having more than 3 C atoms can be straight chain, branched and/or cyclic and may contain spiro links or condensed rings.

Throughout the application, unless stated explicitly otherwise, the term "aryl and heteroaryl groups" encompass groups, which can be monocyclic or polycyclic, i.e. they can have one ring (such as, for example, phenyl) or two or more rings, which may also be fused (such as, for example,

- 9 -

naphthyl) or covalently linked (such as, for example, biphenyl), or contain a combination of fused and linked rings.

Heteroaryl groups contain one or more heteroatoms, preferably selected 5 from O, N, S and Se. Particular preference is given to mono-, bi- or tricyclic aryl groups having 6 to 25 C atoms and mono-, bi- or tricyclic heteroaryl groups having 2 to 25 C atoms, which optionally contain fused rings, and which are optionally substituted. Preference is furthermore given to 5, 6 or 10 7-membered aryl and heteroaryl groups, in which, in addition, one or more CH groups may be replaced by N, S or O in such a way that O atoms and/or S atoms are not linked directly to one another. Preferred aryl groups are, for example, phenyl, biphenyl, terphenyl, [1,1':3',1"]¬¬terphenyl-2'-yl, naphthyl, anthracene, binaphthyl, phenanthrene, pyrene, dihydropyrene, 15 chrysene, perylene, tetracene, pentacene, benzopyrene, fluorene, indene, indenofluorene, spirobifluorene, more preferably 1,4- phenylene, 4,4'biphenylene, 1, 4-tephenylene.

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Preferred heteroaryl groups are, for example, 5 membered rings, such as pyrrole, pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, furan, thiophene, selenophene, oxazole, isoxazole, 1,2 thiazole, 1,3-thiazole, 1,2,3-oxadiazole, 1,2,4 oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 6 membered rings, such as pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, or condensed groups, such as indole, iso-indole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, benzothiazole, benzofuran, isobenzofuran, dibenzofuran, quinoline, isoquinoline, pteridine, benzo-5,6-quinoline, benzo-6,7-quino¬line, benzo-7,8-quinoline, benzoisoquinoline, acridine, phenothiazine, phenoxazine, benzopyridazine, benzopyrimidine,

WO 2018/073459 - 10 -

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quinoxaline, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthridine, phenanthroline, thieno[2,3b]thiophene, thieno[3,2b]-thiophene, dithienothiophene, isobenzothiophene, dibenzothiophene, benzothiadiazothiophene, or combinations of these groups. The heteroaryl groups may also be substituted by alkyl, alkoxy, thioalkyl, fluorine, fluoroalkyl or further aryl or heteroaryl groups.

PCT/EP2018/053801

In the context of this application, the term "(non-aromatic) alicyclic and heterocyclic groups" encompass both saturated rings, i.e. those that contain exclusively single bonds, and partially unsaturated rings, i.e. those that may also contain multiple bonds. Heterocyclic rings contain one or more heteroatoms, preferably selected from Si, O, N, S and Se. The (nonaromatic) alicyclic and heterocyclic groups can be monocyclic, i.e. contain only one ring (such as, for example, cyclohexane), or polycyclic, i.e. contain a plurality of rings (such as, for example, decahydro-naphthalene or bicyclooctane). Particular preference is given to saturated groups. Preference is furthermore given to mono-, bi- or tricyclic groups having 3 to 25 C atoms, which optionally contain fused rings and that are optionally substituted. Preference is furthermore given to 5-, 6-, 7- or 8-membered carbocyclic groups in which, in addition, one or more C atoms may be replaced by Si and/or one or more CH groups may be replaced by N and/or one or more non-adjacent CH<sub>2</sub> groups may be replaced by -O- and/or -S-. Preferred alicyclic and heterocyclic groups are, for example, 5-membered groups, such as cyclopentane, tetrahydrofuran, tetrahydrothiofuran, pyrrolidine, 6-membered groups, such as cyclohexane, silinane, cyclohexene, tetrahydropyran, tetrahydrothiopyran, 1,3-dioxane, 1,3dithiane, piperidine, 7-membered groups, such as cycloheptane, and fused groups, such as tetrahydronaphthalene, decahydronaphthalene, indane, bicyclo[1.1.1] pentane-1,3-diyl, bicyclo[2.2.2] octane-1,4-diyl, spiro[3.3]heptane-2,6-diyl, octahydro-4,7-methanoindane-2,5-diyl, more preferably 1,4-cyclohexylene 4,4'- bicyclohexylene, 3,17-hexadecahydrocyclopenta[a]phenanthrene, optionally being substituted by one or more

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identical or different groups L. Especially preferred aryl-, heteroaryl-, alicyclic- and heterocyclic groups are 1,4-phenylene, 4,4'-biphenylene, 1,4-terphenylene, 1,4-cyclohexylene, 4,4'- bicyclohexylene, and 3,17-hexadecahydro-cyclopenta[a]-phenanthrene, optionally being substituted by one or more identical or different groups L.

Preferred substituents (L) of the above-mentioned aryl-, heteroaryl-, alicyclic- and heterocyclic groups are, for example, solubility-promoting groups, such as alkyl or alkoxy and electron-withdrawing groups, such as fluorine, nitro or nitrile.

Preferred substituents, also referred to as "L" below, are, for example, F, Cl, Br, I, -OH, -CN, -NO<sub>2</sub>, -NCO, -NCS, -OCN, -SCN, -C(=O)N(R<sup>x</sup>)<sub>2</sub>, -C(=O)Y<sup>x</sup>, -C(=O)R<sup>x</sup>, -C(=O)OR<sup>x</sup>, -N(R<sup>x</sup>)<sub>2</sub>, in which R<sup>x</sup> has the above-mentioned meaning, and above Y<sup>x</sup> denotes halogen, optionally substituted silyl, optionally substituted aryl or heteroaryl having 4 to 40, preferably 4 to 20 ring atoms, and straight-chain or branched alkyl, alkenyl, alkinyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having 1 to 25 C atoms, in which one or more H atoms may optionally be replaced by F or Cl.

"Substituted silyl or aryl" preferably means silyl or aryl substituted by halogen, -CN, R<sup>y</sup>, -OR<sup>y</sup>, -CO-R<sup>y</sup>, -CO-O-R<sup>y</sup>, -O-CO-R<sup>y</sup> or -O-CO-O-R<sup>y</sup>, in which R<sup>y</sup> denotes H, a straight-chain, branched or cyclic alkyl chain having 1 to 12 C atoms.

In the formulae shown above and below, a substituted phenylene ring

is preferably 
$$\longrightarrow$$
  $\downarrow$  ,  $\longrightarrow$  ,  $\longrightarrow$  ,  $\longrightarrow$  ,  $\longrightarrow$  ,

$$\stackrel{L}{\longleftarrow} , \qquad \stackrel{L}{\longleftarrow} \qquad \text{or} \qquad \stackrel{L}{\longleftarrow}$$

"Halogen" denotes F, Cl, Br or I, preferably F or Cl, more preferably F.

- Above and below, the terms "alkyl", "aryl", "heteroaryl", etc., also encompass polyvalent groups, for example alkylene, arylene, heteroarylene, etc.
- The term "aryl" denotes an aromatic carbon group or a group derived there from.
  - The term "heteroaryl" denotes "aryl" in accordance with the above definition containing one or more heteroatoms.

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Preferred alkyl groups are, for example, methyl, ethyl, n propyl, isopropyl, n butyl, isobutyl, s butyl, t butyl, 2 methylbutyl, n pentyl, s pentyl, cyclopentyl, n hexyl, cyclohexyl, 2 ethylhexyl, n heptyl, cycloheptyl, n octyl, cyclooctyl, n nonyl, n decyl, n undecyl, n dodecyl, dodecanyl, trifluoromethyl, perfluoro-n-butyl, 2,2,2-trifluoroethyl, perfluorooctyl, per¬fluorohexyl, etc.

Preferred alkoxy groups are, for example, methoxy, ethoxy, 2-methoxyethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, 2methylbutoxy, n-pentoxy, n-hexoxy, n-heptoxy, n-octoxy, n-nonoxy, n-decoxy, n-undecoxy, n-dodecoxy.

- Preferred alkenyl groups are, for example, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl.
- Preferred alkynyl groups are, for example, ethynyl, propynyl, butynyl, pentynyl, hexynyl, octynyl.

Preferred amino groups are, for example, dimethylamino, methylamino, methylphenylamino, phenylamino.

"Polymerisable groups" (P) are preferably selected from groups containing a C=C double bond or C≡C triple bond, and groups which are suitable for polymerisation with ring opening, such as, for example, oxetane or epoxide groups.

Preferably, polymerisable groups (P) are selected from the group

consisting of 
$$CH_2=CW^1$$
- $COO$ -,  $CH_2=CW^1$ - $CO$ -,  $W^2HC$   $CH$   $-$ 

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$$W^2$$
  $(CH_2)_{k1}$ -O-,  $W^4$   $(CH_2)_{\overline{k4}}$  ,  $CH_2$ = $CW^2$ - $(O)_{k3}$ -,

W<sup>1</sup> denotes H, F, Cl, CN, CF<sub>3</sub>, phenyl or alkyl having 1 to 5 C atoms, in particular H, F, Cl or CH<sub>3</sub>,

- W<sup>2</sup> denotes H or alkyl having 1 to 5 C atoms, in particular H, methyl, ethyl or n-propyl,
- $k_1$ ,  $k_2$  and  $k_3$  each, independently of one another, denote 0 or 1,  $k_3$  preferably denotes 1, and  $k_4$  is an integer from 1 to 10.

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Particularly preferred polymerizable groups P are CH<sub>2</sub>=CH-COO-, CH<sub>2</sub>=C(CH<sub>3</sub>)-COO-, CH<sub>2</sub>=CF-COO-, CH<sub>2</sub>=CH-, CH<sub>2</sub>=CH-O-,

(CH<sub>2</sub>=CH)<sub>2</sub>CH-OCO-, (CH<sub>2</sub>=CH)<sub>2</sub>CH-O-, W<sup>2</sup>HC 
$$\stackrel{\frown}{--}$$
CH  $\stackrel{\frown}{-}$  and

- 25  $W^2$   $(CH_2)_{k1}$ -O-, in which  $W^2$  denotes H or alkyl having 1 to 5 C atoms, in particular H, methyl, ethyl or n-propyl,
- Further preferred polymerizable groups (P) are, vinyl, vinyloxy, acrylate, methacrylate, fluoroacrylate, chloroacrylate, oxetane and epoxide, most preferably acrylate or methacrylate, in particular acrylate.
- Preferably, all multireactive polymerisable compounds and sub-formulae thereof contain instead of one or more radicals P-Sp-, one or more

branched radicals containing two or more polymerisable groups P (multireactive polymerisable radicals).

Suitable radicals of this type, and polymerisable compounds containing them, are described, for example, in US 7,060,200 B1 or US 2006/0172090 A1.

Particular preference is given to multireactive polymerisable radicals selected from the following formulae:

	-X-alkyl-CHP <sup>x</sup> -CH <sub>2</sub> -CH <sub>2</sub> P <sup>y</sup>	l*a
15	-X-alkyl-C(CH <sub>2</sub> P <sup>x</sup> )(CH <sub>2</sub> P <sup>y</sup> )-CH <sub>2</sub> P <sup>z</sup>	l*b
	-X-alkyl-CHP*CHP <sup>y</sup> -CH <sub>2</sub> P <sup>z</sup>	l*c
20	-X-alkyl-C(CH <sub>2</sub> P <sup>x</sup> )(CH <sub>2</sub> P <sup>y</sup> )-C <sub>aa</sub> H <sub>2aa+1</sub>	I*d
	-X-alkyl-CHP <sup>x</sup> -CH₂P <sup>y</sup>	l*e
25	-X-alkyl-CHP <sup>x</sup> P <sup>y</sup>	l*f
	-X-alkyl-CP <sup>x</sup> P <sup>y</sup> -C <sub>aa</sub> H <sub>2aa+1</sub>	l*g
30	-X-alkyl-C(CH <sub>2</sub> P <sup>v</sup> )(CH <sub>2</sub> P <sup>w</sup> )-CH <sub>2</sub> OCH <sub>2</sub> -C(CH <sub>2</sub> P <sup>x</sup> )(CH <sub>2</sub> Py)CH <sub>2</sub> P <sup>z</sup>	I*h
	-X-alkyl-CH((CH <sub>2</sub> ) <sub>aa</sub> P $^{x}$ )((CH <sub>2</sub> ) <sub>bb</sub> P $^{y}$ )	l*i
	-X-alkyl-CHP <sup>x</sup> CHP <sup>y</sup> -C <sub>aa</sub> H <sub>2aa+1</sub>	l*k

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in which

WO 2018/073459

alkyl denotes a single bond or straight-chain or branched alkylene having 1 to 12 C atoms, in which one or more non-adjacent CH<sub>2</sub> groups may each be replaced, independently of one another, by -C(Rx)=C(Rx)-, -C=C-, -N(Rx)-, -O-, -S-, -CO-, -CO-O-, -O-CO-, 5 -O-CO-O- in such a way that O and/or S atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by F, Cl or CN, where Rx has one the above-mentioned meaning,

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aa and bb each, independently of one another, denote 0, 1, 2, 3, 4, 5 or 6,

Χ has one of the meanings indicated for X', and

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P<sup>v</sup> to P<sup>z</sup> each, independently of one another, have one of the meanings indicated above for P.

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Preferred spacer groups Sp are selected from the formula Sp'-X', so that the radical "P-Sp-" conforms to the formula "P-Sp'-X'-", where

Sp'

denotes alkylene having 1 to 20, preferably 1 to 12 C atoms, which is optionally mono- or polysubstituted by F, Cl, Br, I or CN and in which, in addition, one or more non-adjacent CH<sub>2</sub> groups may each be replaced, independently of one another, by -O-, -S-, -NH-, -NR<sup>xx</sup>-, -SiR<sup>xx</sup>R<sup>yy</sup>-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -NR<sup>xx</sup>-CO-O-, -O-CO-NR<sup>0xx</sup>-, -NR<sup>xx</sup>-CO-NR<sup>yy</sup>-, -CH=CH- or -C≡C- in such a way that O and/or S atoms are not linked directly to one another.

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X' denotes -O-, -S-, -CO-, -COO-, -O-COO-, -CO-NRxx-, -NR<sup>xx</sup>-CO-, -NR<sup>xx</sup>-CO-NR<sup>yy</sup>-, -OCH<sub>2</sub>-, -CH<sub>2</sub>O-, -SCH<sub>2</sub>-, -CH<sub>2</sub>S-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CF<sub>2</sub>S-, -SCF<sub>2</sub>-, -CF<sub>2</sub>CH<sub>2</sub>-,

- 17 -

-CH<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CH=N-, -N=CH-, -N=N-, -CH=CR<sup>xx</sup>-, -CY<sup>xx</sup>=CY<sup>xx</sup>-, -C $\equiv$ C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

R<sup>xx</sup> and R<sup>yy</sup> each, independently of one another, denote H or alkyl having 1 to 12 C atoms, and

Y<sup>xx</sup> and Y<sup>yy</sup> each, independently of one another, denote H, F, Cl or CN.

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X' is preferably -O-, -S- -CO-, -COO-, -O-COO-, -CO-NR\*x-, -NR\*x-CO-, -NR\*x-CO-NR\*yy- or a single bond.

- Typical spacer groups Sp' are, for example,  $-(CH_2)_{p1}$ -,  $-(CH_2CH_2O)_{q1}$   $CH_2CH_2$ -,  $-CH_2CH_2$ -S- $-CH_2CH_2$ -,  $-CH_2CH_2$ -NH- $-CH_2CH_2$  or  $-(SiR^{xx}R^{yy}-O)_{p1}$ -, in which p1 is an integer from 1 to 12, q1 is an integer from 1 to 3, and  $-R^{xx}$  and  $-R^{yy}$  have the above-mentioned meanings.
- Particularly preferred groups -X'-Sp'- are -(CH<sub>2</sub>)<sub>p1</sub>-, -O-(CH<sub>2</sub>)<sub>p1</sub>-, -OCO-(CH<sub>2</sub>)<sub>p1</sub>-, in which p1 is an integer from 1 to 12.
- Particularly preferred groups Sp' are, for example, in each case straightchain, methylene, ethylene, propylene, butylene, pentylene, hexylene,
  heptylene, octylene, nonylene, decylene, undecylene, dodecylene,
  octadecylene, ethyleneoxyethylene, methyleneoxybutylene,
  ethylenethioethylene, ethylene-N-methyliminoethylene, 1-methylalkylene,
  ethenylene, propenylene and butenylene.

The birefringence  $\Delta n$  herein is defined by the following equation  $\Delta n = n_e - n_o$ 

wherein  $n_e$  is the extraordinary refractive index and  $n_o$  is the ordinary refractive index and the effective average refractive index  $n_{av.}$  is given by the following equation

$$n_{av.} = [(2 n_o^2 + n_e^2)/3]^{1/2}$$

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The extraordinary refractive index  $n_e$  and the ordinary refractive index  $n_o$  can be measured e.g. using a modified Abbe refractometer in accordance to "Merck Liquid Crystals, Physical Properties of Liquid Crystals", Status Nov. 1997, Merck KGaA, Germany.

The retardation (R( $\lambda$ )) of a material can be measured using a spectroscopic ellipsometer, for example the M2000 spectroscopic ellipsometer manufactured by J. A. Woollam Co., This instrument is capable of measuring the optical retardance in nanometres of a birefringent sample e.g. Quartz over a range of wavelengths typically ranging from 370 nm to 2000 nm.

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A method for carrying out these measurements was presented at the National Physics Laboratory (London, UK) by N. Singh in October 2006 and entitled "Spectroscopic Ellipsometry, Part1-Theory and Fundamentals, Part 2 – Practical Examples and Part 3 - measurements". In accordance with the measurement procedures described in Retardation Measurement (RetMeas) Manual (2002) and Guide to WVASE (2002) (Woollam Variable Angle Spectroscopic Ellipsometer) published by J. A. Woollam Co. Inc (Lincoln, NE, USA). Unless stated otherwise, this method is used to determine the retardation of the materials, films and devices described in this invention.

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The term "transparent" in the context of this application is taken to mean that the transmission of light through the device is at least 65 % of the incident light, more preferably at least 80 %, even more preferably at least 90 %.

Visible light is electromagnetic radiation that has wavelength in a range from about above 400 nm to about 800 nm. Ultraviolet (UV) light is electromagnetic radiation with a wavelength in a range from about 200 nm to about below 400 nm.

The Irradiance ( $E_e$ ) or radiation power is defined as the power of electromagnetic radiation ( $d\theta$ ) per unit area (dA) incident on a surface:

10  $E_e = d\theta/dA$ .

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The radiant exposure or radiation dose (H<sub>e</sub>), is defined as the irradiance or radiation power (E<sub>e</sub>) per time (t):

 $H_e = E_e \cdot t$ .

All temperatures, such as, for example, the melting point T(C,N) or T(C,S), the transition from the smectic (S) to the nematic (N) phase T(S,N) and the clearing point T(N,I) of the liquid crystals, are quoted in degrees Celsius. All temperature differences are quoted in differential degrees.

The term "clearing point" means the temperature at which the transition between the mesophase with the highest temperature range and the isotropic phase occurs.

All concentrations are quoted in percent by weight and relate to the respective mixture as a whole, all temperatures are quoted in degrees.

Celsius and all temperature differences are quoted in differential degrees.

In the present application the term "dielectrically positive" is used for compounds or components with  $\Delta\epsilon$  > 3.0, "dielectrically neutral" with -1.5  $\leq$   $\Delta\epsilon \leq$  3.0 and "dielectrically negative" with  $\Delta\epsilon$  < -1.5.

- 20 -

 $\Delta\epsilon$  is determined at a frequency of 1 kHz and at 20°C. The dielectric anisotropy of the respective compound is determined from the results of a solution of 10 % of the respective individual compound in a nematic host mixture. In case the solubility of the respective compound in the host medium is less than 10 % its concentration is reduced by a factor of 2 until the resultant medium is stable enough at least to allow the determination of its properties at a given temperature, preferably at 20°C. In a preferred embodiment, the concentration is kept at least at 5 %, however, in order to keep the significance of the results a high as possible. The capacitance of the test mixtures are determined both in a cell with homeotropic and with homogeneous alignment. The cell gap of both types of cells is approximately 20  $\mu$ m. The voltage applied is a rectangular wave with a frequency of 1 kHz and a root mean square value typically of 0.5 V to 1.0 V; however, it is always selected to be below the capacitive threshold of the respective test mixture.

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 $\Delta\epsilon$  is defined as  $(\epsilon_{\parallel} - \epsilon_{\perp})$ , whereas  $\epsilon_{av.}$  is  $(\epsilon_{\parallel} + 2 \epsilon_{\perp})$  / 3. The dielectric permittivity of the compounds is determined from the change of the respective values of a host medium upon addition of the compounds of interest. The values are extrapolated to a concentration of the compounds of interest of 100 %. A typical host medium is ZLI-4792 or BL-087 both commercially available from Merck, Darmstadt.

Unless the context clearly indicates otherwise, as used herein plural forms of the terms herein are to be construed as including the singular form and vice versa.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and are not intended to (and do not) exclude other components. On the other hand,

- 21 -

the word "comprise" also encompasses the term "consisting of" but is not limited to it.

Throughout the description and claims of this specification, the words "obtainable" and "obtained" and variations of the words, mean "including but not limited to", and are not intended to (and do not) exclude other components. On the other hand, the word "obtainable" also encompasses the term "obtained" but is not limited to it.

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### **DETAILED DESCRIPTION**

In a preferred embodiment of the invention, the utilized substrate is substantially transparent. However, it is likewise preferred that the utilized substrate is optically opaque. The skilled person commonly knows materials suitable for the purpose of the present invention.

In accordance with the invention, the substrate preferably consists of a polymeric or plastic material, or of metal oxides, for example ITO, or of glass or quartz, more preferably, the substrate consists glass or plastic.

A suitable and preferred plastic substrate is for example a film of cyclo olefin polymer (COP), cyclic olefin copolymer (COC), polyester such as polyethyleneterephthalate (PET) or polyethylene-naphthalate (PEN), polyeinylalcohol (PVA), polycarbonate (PC) or triacetylcellulose (TAC), very preferably a PET or TAC film. PET films are, for example, commercially available under the trade name Melinex ® from DuPont Teijin Films. COP films are commercially available for example from ZEON Chemicals L.P. under the trade name Zeonor ® or Zeonex ®. COC films are commercially available for example from TOPAS Advanced Polymers Inc. under the trade name Topas ®.

WO 2018/073459 - 22 -

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In a further preferred embodiment of the invention, the substrate is flexible and the device according to the invention is consequently flexible and bendable and can be rolled up, for example.

PCT/EP2018/053801

In a preferred embodiment, the device according to the present invention comprises an electrode structure, which is capable to allow the application of an electric field, which is substantially parallel to the substrate main plane or the polymer film, or has at least a substantial component in that direction.

In a preferred embodiment, the electrode structure is preferably placed on the substrate and is therefore protected from mechanical damage. Unless the entire display assembly is intended to be flexible, preferably the electrodes may be formed on a low cost rigid substrate, which will further increase the durability of the device.

In a preferred embodiment, the substrate carries patterns of parallel electrodes, for example, in a comb-like electrode arrangement.

Other suitable electrode structures are commonly known to the expert and for example disclosed in WO 2004/029697 A1.

In another preferred embodiment, one of the substrates includes a pixel electrode and a common electrode for generating an electric field substantially parallel to a surface of the first substrate in the pixel region.

Different kinds of devices having at least two electrodes on one substrate are known to the skilled person wherein the most important difference is that either both the pixel electrode and the common electrode are structured, as it is typical for IPS displays, or only the pixel electrode is structured and the common electrode is unstructured, which is the case for FFS displays.

- 23 -

In a further preferred embodiment, the in-plane electrode structure is selected from interdigitated electrodes, IPS electrodes, FFS electrodes or comb like electrodes, preferably interdigitated electrodes or comb like electrodes. In this connection, document WO 2008/104533 A1 describes arrangements where the electrodes are arranged as an IPS electrode and arrangements where an additional base electrode is disposed on the same substrate, as a fringe-field switching (FFS) electrode.

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Suitable electrode materials are commonly known to the expert, as for example electrodes made of conductive polymers, metal or metal oxides, such as, for example transparent indium tin oxide (ITO), which is preferred according to the present invention.

In a preferred embodiment, the electrodes can have a circular crosssection, in the form of a solid wire or a cylinder, or the electrodes can have a rectangular or an almost rectangular cross section. Especially preferred is a rectangular or almost rectangular cross section of the electrodes.

The gap between the electrodes is preferably in the range from approximately 1  $\mu m$  to approximately 50  $\mu m$ , more preferably in the range from approximately 5  $\mu m$  to approximately 25  $\mu m$ , and even more preferably in the range from approximately 7  $\mu m$  to approximately 12  $\mu m$ 

The width of the electrodes is preferably in the range from approximately 1  $\mu m$  to approximately 50  $\mu m$ , more preferably in the range from approximately 5  $\mu m$  to approximately 25  $\mu m$ , and even more preferably in the range from approximately 7  $\mu m$  to approximately 12  $\mu m$ 

As commonly known, the electrode structure can typically be provided on the substrate by current lithographic techniques.

In a preferred embodiment, the electrodes of the light modulation element are connected with an electrically switching element, such as a thin film transistor (TFT) or a thin film diode (TFD).

In a preferred embodiment, the electrodes are located under the liquid crystalline polymer film or alignment layer, not being touched by the user.

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In a preferred embodiment, the electrode structure is in direct contact with the liquid crystalline polymer film.

In another preferred embodiment, the substrate and/or the electrode structure is covered with a thin alignment layer to control the alignment of the liquid crystal monomers prior to polymerization.

In a preferred embodiment, the liquid crystalline polymer film is obtainable, preferably obtained, from a polymerisable LC medium comprising one or more multi-, di- or monoreactive mesogenic compounds.

Suitable multi-, di- or monoreactive mesogenic compounds are for example disclosed in WO 93/22397, EP 0 261 712, DE 195 04 224, WO 95/22586, WO 97/00600, GB 2 351 734, WO 98/00475 or WO 98/04651.

The compounds disclosed in these documents, however, are to be regarded merely as examples that shall not limit the scope of this invention.

In a preferred embodiment, the liquid crystalline polymer film is obtainable from a polymerisable LC medium comprising one or more multi-, di- or monoreactive mesogenic compounds having a dipole moment in the range from 2 to 8 Debye.

Typically, the dipole moment can be determined from dielectric measurements as commonly known by the skilled person.

In a preferred embodiment, the liquid crystalline polymer film is obtainable, preferably obtained from a polymerisable LC medium comprising, preferably consisting of, one or more multi- or direactive mesogenic compounds and optionally one or more monoreactive mesogenic compounds.

In a preferred embodiment, one or more di- or multireactive mesogenic compounds are selected of formula DRM

DRM

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WO 2018/073459

P<sup>1</sup> and P<sup>2</sup> independently of each other denote a polymerisable group,

Sp¹ and Sp² independently of each other are a spacer group or a single bond, and

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MG is a mesogenic group, which is preferably selected of formula MG

 $-(A^1-Z^1)_n-A^2-$ 

MG

wherein

A¹ and A² denote, in case of multiple occurrence independently of one another, an aromatic or alicyclic group, which optionally contains one or more heteroatoms selected from N, O and S, and is optionally mono- or polysubstituted by L¹,

denotes, in case of multiple occurrence independently of one another, P¹-Sp¹-, F, Cl, Br, I, -CN, -NO<sub>2</sub>, -NCO, -NCS, -OCN,

-SCN, -C(=O)NR<sup>00</sup>R<sup>000</sup>, -C(=O)OR<sup>00</sup>, -C(=O)R<sup>00</sup>, -NR<sup>00</sup>R<sup>000</sup>, -OH, -SF<sub>5</sub>, optionally substituted silyl, aryl or heteroaryl with 1 to 12, preferably 1 to 6 C atoms, and straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12, preferably 1 to 6 C atoms, wherein one or more H atoms are optionally replaced by F or Cl,

10  $Z^1$ 

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denotes, in case of multiple occurrence independently of one another, -O-, -S-, -CO-, -COO-, -OCO-, -S-CO-, -CO-S-, -O-COO-, -CO-NR $^{00}$ -, -NR $^{00}$ -CO-, -CO-NR $^{00}$ -, -NR $^{00}$ -CO-O-, -O-CO-NR $^{00}$ -, -OCH $_2$ -, -CH $_2$ O-, -SCH $_2$ -, -CH $_2$ S-, -CF $_2$ O-, -OCF $_2$ -, -CF $_2$ S-, -SCF $_2$ -, -CH $_2$ CH $_2$ -, -(CH $_2$ )n1, -CF $_2$ CH $_2$ -, -CH $_2$ CF $_2$ -, -CF $_2$ CF $_2$ -, -CH=N-, -N=CH-, -N=N-, -CH=CR $^{00}$ -, -CY $^1$ =CY $^2$ -, -C $\equiv$ C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

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R<sup>00</sup> and R<sup>000</sup> independently of each other denote H or alkyl with 1 to 12 C-atoms,

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Y<sup>1</sup> and Y<sup>2</sup> independently of each other denote H, F, Cl or CN,

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n is 1, 2, 3 or 4, preferably 1 or 2, most preferably 2,

n1

is an integer from 1 to 10, preferably 1, 2, 3 or 4.

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Preferred groups A<sup>1</sup> and A<sup>2</sup> include, without limitation, furan, pyrrol, thiophene, oxazole, thiazole, thiadiazole, imidazole, phenylene, cyclohexylene, bicyclooctylene, cyclohexenylene, pyridine, pyrimidine, pyrazine, azulene, indane, fluorene, naphthalene, tetrahydronaphthalene, anthracene, phenanthrene and dithienothiophene, all of which are unsubstituted or substituted by 1, 2, 3 or 4 groups L<sup>1</sup> as defined above.

PCT/EP2018/053801

Particular preferred groups A¹ and A² are selected from 1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl, thiophene-2,5-diyl, naphthalene-2,6-diyl, 1,2,3,4-tetrahydro-naphthalene-2,6-diyl, indane-2,5-diyl, bicyclooctylene or 1,4-cyclohexylene wherein one or two non-adjacent CH₂ groups are optionally replaced by O and/or S, wherein these groups are unsubstituted or substituted by 1, 2, 3 or 4 groups L¹ as defined above.

- 10 Especially preferred compounds of formula DRM are selected from trireactive compounds wherein one of L¹ denotes P¹-Sp¹-. Further preferred compounds of formula DRM are selected from multireactive compounds wherein two or more of L¹ denotes P¹-Sp¹-.
- Particular preferred groups Z¹ are in each occurrence independently from another preferably selected from -COO-, -OCO-, -CH₂CH₂-, -CF₂O-, -OCF₂-, -C≡C-, -CH=CH-,-OCO-CH=CH-, -CH=CH-COO-, or a single bond,
- 20 Preferably one or more direactive mesogenic compounds of formula DRM are selected from the following formulae:

$$25 \qquad P^{0}(CH_{2})_{x}(O)_{z} \xrightarrow{(L)_{r}} COO \xrightarrow{(L)_{r}} OCO \xrightarrow{(L)_{r}} (O)_{z}(CH_{2})_{y}P^{0} \qquad DRMa1$$

$$P^{0}(CH_{2})_{x}(O)_{z}$$
  $\longrightarrow$   $OOC$   $\longrightarrow$   $COO$   $\longrightarrow$   $OO_{z}(CH_{2})_{y}P^{0}$   $ORMa3$ 

PCT/EP2018/053801

$$P^{0}(CH_{2})_{x}(O)_{z} \xrightarrow{(L)_{r}} CH_{2}CH_{2} \xrightarrow{(L)_{r}} CH_{2}CH_{2} \xrightarrow{(L)_{r}} OO_{z}(CH_{2})_{y}P^{0} DRMa4$$

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$$P^{0}(CH_{2})_{x}(O)_{z}$$
  $CH=CH-COO$   $CH=CH-COO$   $CH=CH-COO_{z}(CH_{2})_{y}P^{0}$   $DRMa6$ 

$$P^{0}(CH_{2})_{x+1}OCOO - COO - COO(CH_{2})_{y+1}P^{0} DRMa7$$

$$P^{0}(CH_{2})_{x}(O)_{z}$$
  $H$   $COO \leftarrow H$   $OCO \leftarrow H$ 

20  $P^{0}(CH_{2})_{x}(O)_{z} \xrightarrow{H} COO \xrightarrow{L)_{r}} OCO \xrightarrow{H} (O)_{z}(CH_{2})_{y}P^{0} \qquad DRMc$ 

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$$P^{0}(CH_{2})_{x}(O)_{z} \xrightarrow{H} COO \xrightarrow{L)_{r}} OCO \xrightarrow{L)_{r}} (O)_{z}(CH_{2})_{y}P^{0} \qquad DRMd$$

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$$P^{0}(CH_{2})_{x+1}OCOO - H OCO - COO(CH_{2})_{y+1}P^{0} DRMe$$

wherein

is, in case of multiple occurrence independently of one another, a polymerisable group, preferably an acryl, methacryl, oxetane,

epoxy, vinyl, heptadiene, vinyloxy, propenyl ether or styrene group,

- in case of multiple occurrence independently of one another, selected from F, Cl, CN or optionally halogenated alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 5 C atoms,
- 10 r is 0, 1, 2, 3 or 4,
  - x and y are independently of each other 0 or identical or different integers from 1 to 12,
- z is each and independently, 0 or 1, with z being 0 if the adjacent x or y is 0.
- Especially preferred are compounds of formula DRMa1, DRMa2 and DRMa3, in particular those of formula DRMa1.

In another preferred embodiment, the liquid crystalline polymer film is obtainable, preferably obtained, from a polymerisable LC medium comprising, additionally to one or more compounds of formula DRM, one or more monoreactive mesogenic compounds.

In a preferred embodiment, one or more monoreactive compounds are selected from compounds of formula MRM,

P<sup>1</sup>-Sp<sup>1</sup>-MG-R MRM

wherein

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35 P<sup>1</sup> denotes a polymerisable group,

WO 2018/073459

- 30 -

Sp<sup>1</sup> is a spacer group or a single bond,

MG is a mesogenic group, which is preferably

selected of formula MG

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 $-(A^1-Z^1)_n-A^2-$  MG

wherein

 $L^2$ 

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A¹ and A² denote, in case of multiple occurrence independently of one another, an aromatic or alicyclic group, which optionally contains one or more heteroatoms selected from N, O and S,

PCT/EP2018/053801

and is optionally mono- or polysubstituted by L<sup>2</sup>,

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denotes, in case of multiple occurrence independently of one another, F, Cl, Br, I, -CN, -NO<sub>2</sub>, -NCO, -NCS, -OCN, -SCN, -C(=O)NR<sup>00</sup>R<sup>000</sup>, -C(=O)OR<sup>00</sup>, -C(=O)R<sup>00</sup>, -NR<sup>00</sup>R<sup>000</sup>, -OH, -SF<sub>5</sub>, optionally substituted silyl, aryl or heteroaryl with 1 to 12, preferably 1 to 6 C atoms, and straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12, preferably 1 to 6 C atoms, wherein one or more H atoms are optionally

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replaced by F or Cl,

 $Z^1$ 

denotes, in case of multiple occurrence independently of one another, -O-, -S-, -CO-, -COO-, -OCO-, -S-CO-, -CO-S-, -O-COO-, -CO-NR<sup>00</sup>-, -NR<sup>00</sup>-CO-, -NR<sup>00</sup>-CO-NR<sup>00</sup>, -NR<sup>00</sup>-CO-O-, -O-CO-NR<sup>00</sup>-, -OCH<sub>2</sub>-, -CH<sub>2</sub>O-, -SCH<sub>2</sub>-, -CH<sub>2</sub>S-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CF<sub>2</sub>S-, -SCF<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -(CH<sub>2</sub>)<sub>n1</sub>, -CF<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CF<sub>2</sub>-, -CH<sub>2</sub>CF<sub>2</sub>-, -CH<sub>2</sub>N-, -N=CH-, -N=N-,

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-CH=CR $^{00}$ -, -CY $^{1}$ =CY $^{2}$ -, -C $\equiv$ C-, -CH=CH-COO-,

-OCO-CH=CH- or a single bond,

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 $\mathsf{R}^{00}$  and  $\mathsf{R}^{000}$  independently of each other denote H or alkyl with 1 to 12 C-atoms,

5 Y<sup>1</sup> and Y<sup>2</sup> independently of each other denote H, F, Cl or CN,

n is 1, 2, 3 or 4, preferably 1 or 2, most preferably 2,

10 n1 is an integer from 1 to 10, preferably 1, 2, 3 or 4, and

 $R \qquad \qquad \text{F, Cl, Br, I, -CN, -NO}_2 \text{, -NCO, -NCS, -OCN, -SCN,} \\ -\text{C(=O)NR}^x\text{R}^y \text{, -C(=O)X, -C(=O)OR}^x \text{, -C(=O)R}^y \text{, -NR}^x\text{R}^y \text{, -OH,} \\ -\text{SR}^x \text{, -SF}_5 \text{, optionally substituted silyl, straight chain or} \\ \text{branched alkyl having 1 to 20, preferably 1 to 12, C atoms,} \\ \text{which is optionally mono- or polysubstituted by F, Cl, Br, I or} \\ \text{CN and wherein, in addition, one or more non-adjacent CH}_2 \\ \text{groups may each be replaced, independently of one another,} \\ \text{by -O-, -S-, -NH-, -N(R}^0)-, -Si(R}^{00}R^{000})-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -S-CO-, -CO-S-, -N(R}^{00})-CO-O-, -O-CO-, -O-CO-,$ 

R<sup>x</sup> and R<sup>y</sup> are independently of each other H or alkyl with 1 to 12 C-atoms.

another,

way that O and/or S atoms are not linked directly to one

In a preferred embodiment, one or more monoreactive mesogenic compounds of formula MRM are selected from the following formulae.

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$$P^{0}$$
- $(CH_{2})_{x}(O)_{z}$   $R^{0}$  MRM1

- 32 -

$$P^0$$
-(CH<sub>2</sub>)<sub>x</sub>(O)<sub>z</sub>  $\longrightarrow$   $COO \xrightarrow{}_{w} H \longrightarrow R^0$ 

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$$P^{0}-(CH_{2})_{x}(O)_{z} \longrightarrow H \longrightarrow R^{0}$$
 MRM3

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$$P^0$$
- $(CH_2)_x(O)_z$   $COO$   $R^0$ 

$$P^{0}(CH_{2})_{x}(O)_{z} \xrightarrow{A^{0}} -COO \xrightarrow{L)_{r}} -COO \xrightarrow{L)_{r}} R^{0}$$
MRM5

$$P^{0}(CH_{2})_{x}(O)_{z}$$
  $COO - COO - R^{0}$  MRM6

$$P^0$$
- $(CH_2)_x(O)_z$   $COO$   $H$   $R^0$  MRM7

$$P^{0}(CH_{2})_{x}(O)_{z} \xrightarrow{(L)_{r}} R^{0} \qquad MRM8$$

- 33 -

$$\mathsf{P}^0(\mathsf{CH}_2)_{\mathsf{x}}(\mathsf{O})_{\mathsf{z}} \underbrace{\hspace{1cm} (\mathsf{L})_{\mathsf{r}}}_{\mathsf{L}} \underbrace{\hspace{1cm} (\mathsf{L})_{\mathsf{r}}}_{\mathsf{R}^0}$$
 MRM10

 $P^{0}\text{-}(CH_{2})_{x}(O)_{z} \xrightarrow{\qquad \qquad \qquad } R^{0}$   $(L) \qquad \qquad (L) \qquad \qquad MRM11$ 

10  $P^0$ -(CH<sub>2</sub>)<sub>x</sub>(O)<sub>z</sub>-COO H H R<sup>0</sup>

 $P^{0}-(CH_{2})_{x}(O)_{z} \xrightarrow{\qquad \qquad \qquad } H \xrightarrow{\qquad \qquad } R^{0}$ 

 $P^{0}(CH_{2})_{x}(O)_{z} \xrightarrow{H} \stackrel{F}{\longrightarrow} R^{0}$ MRM14

 $P^{0}(CH_{2})_{x}(O)_{z}$  H H  $R^{0}$  H H

30  $P^{0}-(CH_{2})_{x}(O)_{z} \xrightarrow{(L)_{r}} CH=CH-COO \xrightarrow{(L)_{r}} Z^{0} \xrightarrow{(L)_{r}} R^{0} \qquad MRM16$ 

- 34 -

$$P^{0}\text{-}(CH_{2})_{x}(O)_{z} \xrightarrow{\text{$(L)_{r}$}} CH\text{=}CH\text{-}COO} \xrightarrow{\text{$(L)_{r}$}} \gamma^{0} \qquad MRM17$$

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$$P^{0}-(CH_{2})_{x}(O)_{z} \xrightarrow{(L)_{r}} COO \xrightarrow{(L)_{r}} CH=CH-COO \xrightarrow{(L)_{r}} R^{0} MRM18$$

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$$P^{0}-(CH_{2})_{x+1}OCOO - Z^{0} - Z^{0}$$

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$$P^{0}(CH_{2})_{x}(O)_{z} \longrightarrow COO \xrightarrow{J_{u}} P^{0} \times Z^{0} \longrightarrow R^{0}$$
 MRM20

$$P^{0}(CH_{2})_{x}(O)_{z} - \underbrace{ \left( \begin{array}{c} \\ \\ \end{array} \right) }_{U} + \underbrace{ \left( \begin{array}{c} \\ \\ \end{array} \right) }_{U} + \underbrace{ \left( \begin{array}{c} \\ \\ \end{array} \right) }_{V} + \underbrace{ \left( \begin{array}{c} \\ \\ \end{array} \right) }_{V} + R^{0}$$

$$\mathsf{P}^0(\mathsf{CH}_2)_{\mathsf{x}}(\mathsf{O})_{\mathsf{z}} - \underbrace{ \left\{ \begin{array}{c} \mathsf{S} \\ \mathsf{J}_{\mathsf{u}} \end{array} \right\} }_{\mathsf{v}} \mathsf{R}^0 \qquad \qquad \mathsf{MRM22}$$

$$P^{0}(CH_{2})_{x}(O)_{z} + \underbrace{Z^{0}}_{u} \underbrace{S}_{y} + \underbrace{Z^{0}}_{v} + \underbrace{Z^{0}}_{v}$$

$$P^{0}(CH_{2})_{x}(O)_{z} + \underbrace{Z^{0}]_{u}} + \underbrace{Z^{0}}_{v} + \underbrace{Z^{0$$

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$$P^{0}(CH_{2})_{x}(O)_{z} - OCO - H - COO - R^{0}$$
MRM25

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$$P^0(CH_2)_x(O)_z$$
  $Z^0$   $U$   $R^0$ 

wherein  $P^0$ , L, r, x, y and z are as defined in formula DRMa-1 to formula DRMe,

- R<sup>0</sup> is a straight-chain or branched alkyl or alkenyl with up to 15 C atoms in which one or more non adjacent CH<sub>2</sub>-groups may be replaced by -O-, -S-, -CO-, -C(O)O-, -O-C(O)-, O-C(O)-O-, or Y<sup>0</sup>, preferably Y<sup>0</sup>,
- Y<sup>0</sup> is F, Cl, CN, NO<sub>2</sub>, OCH<sub>3</sub>, OCN, SCN, SF<sub>5</sub>, or mono- oligo- or polyfluorinated alkyl, alkenyl or alkoxy with 1 to 4 C atoms,
- Z<sup>0</sup> is -COO-, -OCO-, -CH<sub>2</sub>CH<sub>2</sub>-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CH=CH-,-OCO-CH=CH-, -CH=CH-COO-, or a single bond,
- is, in case of multiple occurrence independently of one another, 1,4-phenylene that is unsubstituted or substituted with 1, 2, 3 or 4 groups L, or trans-1,4-cyclohexylene,
- u and v  $\,$  are independently of each other 0, 1 or 2, 35

w is 0 or 1,

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and wherein the benzene and naphthalene rings can additionally be substituted with one or more identical or different groups L.

Further preferred are compounds of formula MRM1, MRM2, MRM3, MRM4, MRM5, MRM6, MRM7, MRM9 and MRM10, more preferred those of formula MRM1, MRM4, MRM6, and MRM7, and in particular those of formulae MRM1and MRM7, and especially those of formulae MRM1and MRM7 wherein R<sup>0</sup> denotes Y<sup>0</sup>.

The proportion of said mono-, di- or multireactive liquid-crystalline compounds in a polymerisable liquid-crystalline material according to the present invention as a whole, is preferably in the range from 30 to 99.9 % by weight, more preferably in the range from 40 to 99.9 % by weight and even more preferably in the range from 50 to 99.9% by weight.

In a preferred embodiment, the proportion of the di- or multireactive polymerisable mesogenic compounds in a polymerisable liquid-crystalline material according to the present invention as a whole, is preferably in the range from 5 to 99 % by weight, more preferably in the range from 10 to 97 % by weight and even more preferably in the range from 15 to 95% by weight.

In another preferred embodiment, the proportion of the monoreactive polymerisable mesogenic compounds in a polymerisable liquid-crystalline material according to the present invention as a whole, is, if present, preferably in the range from 5 to 80% by weight, more preferably in the range from 10 to 75 % by weight and even more preferably in the range from 15 to 70 % by weight.

In another preferred embodiment, the proportion of the multireactive polymerizable mesogenic compounds in a polymerisable liquid-crystalline

- 37 -

material according to the present invention as a whole is, if present, preferably in the range from 1 to 30 % by weight, more preferably in the range from 2 to 20 % by weight and even more preferably in the range from 3 to 10% by weight.

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In another preferred embodiment the polymerisable LC material does not contain polymerizable mesogenic compounds having more than two polymerisable groups.

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In another preferred embodiment the polymerisable LC material does not contain polymerizable mesogenic compounds having less than two polymerisable groups.

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In another preferred embodiment the polymerisable LC material is an achiral material, i.e. it does not contain any chiral polymerizable mesogenic compounds and/or other chiral compounds.

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In a further preferred embodiment, the polymerisable LC material comprises one or more monoreactive mesogenic compound, preferably selected from formula MRM, more preferably selected from compounds of formula MRM-1, and one or more direactive mesogenic compound, preferably selected from formula DRM, more preferably selected from compounds of formula DRMa-1.

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In a further preferred embodiment, the polymerisable LC material comprises one or more monoreactive mesogenic compound, preferably selected from formula MRM, more preferably selected from compounds of formula MRM-7, and one or more direactive mesogenic compound, preferably selected from formula DRM, more preferably selected from compounds of formula DRMa-1.

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- 38 -

In a further preferred embodiment, the polymerisable LC material comprises at least two monoreactive mesogenic compound, preferably selected from compounds of formula MRM more preferably from compounds of formulae MRM-1 and/or MRM-7, and one or more direactive mesogenic compound, preferably selected from formula DRM, more preferably selected from compounds of formula DRMa-1.

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In a further preferred embodiment, the polymerisable LC material

comprises at least two monoreactive mesogenic compounds, preferably selected from compounds of formula MRM more preferably from compounds of formulae MRM-1 and/or MRM-7, and at least two direactive mesogenic compounds, preferably selected from formula DRM, more preferably selected from compounds of formula DRMa-1.

In a further preferred embodiment, the polymerisable LC material comprises at least two direactive mesogenic compounds, preferably selected from formula DRM, more preferably selected from compounds of formula DRMa-1.

The compounds used in the present invention, especially of formula MRM and DRM are either commercially available or can are prepared by methods known per se, as described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for the said reactions. Use can also be made here of variants known per se, which are not mentioned here in greater detail.

In a preferred embodiment, the polymerisable LC material additionally comprises one or more photoinitiators. For polymerising acrylate or methacrylate groups preferably, a radical photoinitiator is used. For polymerising vinyl, epoxide or oxetane groups preferably, a cationic

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- 39 -

PCT/EP2018/053801

photoinitiator is used. It is also possible to use a thermal polymerisation initiator that decomposes when heated to produce free radicals or ions that start the polymerisation.

A typical cationic photoinitiator is for example UVI 6974 (Union Carbide).

As standard photoinitiator for radical polymerisation for example the commercially available Irgacure® or Darocure® (Ciba AG) series can be utilized, in particular, Irgacure 127, Irgacure 184, Irgacure 369, Irgacure 651, Irgacure 817, Irgacure 907, Irgacure 1300, Irgacure, Irgacure 2022, Irgacure 2100, Irgacure 2959, Irgacure Oxe02 or Darocure TPO.

The polymerisable LC material 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.

The lubricants and flow auxiliaries typically include silicon-free, but also silicon-containing polymers, for example polyacrylates or modifiers, low-molecular-weight polydialkylsiloxanes. The modification consists in some of the alkyl groups having been replaced by a wide variety of organic radicals. These organic radicals are, for example, polyethers, polyesters or even long-chain (fluorinated)alkyl radicals, the former being used the most frequently.

The polyether radicals in the correspondingly modified polysiloxanes are usually built up from ethylene oxide and/or propylene oxide units.

Generally, the higher the proportion of these alkylene oxide units in the modified polysiloxane, the more hydrophilic is the resultant product.

Such auxiliaries are, for example, commercially available from Tego as TEGO® Glide 100, TEGO® Glide ZG 400, TEGO® Glide 406, TEGO® Glide 410, TEGO® Glide 411, TEGO® Glide 415, TEGO® Glide 420, TEGO® Glide 435, TEGO® Glide 440, TEGO® Glide 450, TEGO® Glide A 115, TEGO® Glide B 1484 (can also be used as antifoam and deaerator), TEGO® Flow ATF, TEGO® Flow 300, TEGO® Flow 460, TEGO® Flow 425 and TEGO® Flow ZFS 460. Suitable radiation-curable lubricants and flow auxiliaries, which can also be used to improve the scratch resistance, are the products TEGO® Rad 2100, TEGO® Rad 2200, TEGO® Rad 2500, TEGO® Rad 2600 and TEGO® Rad 2700, which are likewise obtainable from TEGO.

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Such-auxiliaries are also available, for example, from BYK as BYK®-300 BYK®-306, BYK®-307, BYK®-310, BYK®-320, BYK®-333, BYK®-341, Byk® 354, Byk®361, Byk®361N, BYK®388.

Such-auxiliaries are also available, for example, from 3M as FC4430®.

Such-auxiliaries are also available, for example, from Cytonix as FluorN®561 or FluorN®562.

Such-auxiliaries are also available, for example, from Merck KGaA as Tivida® FL 2300 and Tivida® FL 2500

The lubricants and flow auxiliaries typically are optionally employed in a proportion of from about 0 to 3.0% by weight, preferably from about 0 to 2.0% by weight, based on the total weight of the polymerisable LC material.

The radiation-curing auxiliaries include, in particular, polysiloxanes having terminal double bonds which are, for example, a constituent of an acrylate

- 41 -

group. Such auxiliaries can be crosslinked by actinic or, for example, electron radiation. These auxiliaries generally combine a number of properties together. In the uncrosslinked state, they can act as antifoams, deaerators, lubricants and flow auxiliaries and/or substrate wetting auxiliaries, while, in the crosslinked state, they increase, in particular, the scratch resistance, for example of coatings or films which can be produced using the compositions according to the invention. The improvement in the gloss properties, for example of precisely those coatings or films, is regarded essentially as a consequence of the action of these auxiliaries as antifoams, deaerators and/or lubricants and flow auxiliaries (in the uncrosslinked state).

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Examples of suitable radiation-curing auxiliaries are the products TEGO® Rad 2100, TEGO® Rad 2200, TEGO® Rad 2500, TEGO® Rad 2600 and TEGO® Rad 2700 available from TEGO and the product BYK®-371 available from BYK.

The radiation-curing auxiliaries are optionally employed in a proportion, if present, from about 0.01 to 5.0% by weight, preferably from about 0.01 to 3.0% by weight, based on the total weight of the polymerisable LC material.

Further adhesion promoters serve to improve the adhesion of two interfaces in contact. It is directly evident from this that essentially the only fraction of the adhesion promoter that is effective is that located at one or the other or at both interfaces. If, for example, it is desired to apply liquid or pasty printing inks, coating compositions or paints to a solid substrate, this generally means that the adhesion promoter must be added directly to the latter or the substrate must be pre-treated with the adhesion promoters (also known as priming), i.e. this substrate is given modified chemical and/or physical surface properties.

If the substrate has previously been primed with a primer, this means that the interfaces in contact are that of the primer on the one hand and of the printing ink or coating composition or paint on the other hand. In this case, not only the adhesion properties between the substrate and the primer, but also between the substrate and the printing ink or coating composition or paint play a part in adhesion of the overall multilayer structure on the substrate.

In view of the widely varying physical and chemical natures of substrates and of printing inks, coating compositions and paints intended, for example, for their printing or coating, the multiplicity of adhesion promoter systems is not surprising.

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- Adhesion promoters based on silanes are, for example, 3aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3aminopropylmethyldiethoxysilane, N-aminoethyl-3aminopropyltrimethoxysilane, N-methyl-3aminopropyltrimethoxysilane, 3-ureidopropyltriethoxysilane, 3methacryloyloxypropyltrimethoxysilane, 3glycidyloxypropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, 3chloropropyltrimethoxysilane and vinyltrimethoxysilane. These and other
  silanes are commercially available from Hüls, for example under the
- Corresponding technical information from the manufacturers of such additives should generally be used or the person skilled in the art can obtain this information in a simple manner through corresponding preliminary experiments.

tradename DYNASILAN®.

If these additives are to be added as adhesion promoters to the polymerisable LC materials according to the invention, their proportion

PCT/EP2018/053801

optionally ranges, if present, from about 0.01 to 5.0% by weight, based on the total weight of the polymerisable LC material. These concentration data serve merely as guidance, since the amount and identity of the additive are determined in each individual case by the nature of the substrate and of the printing/coating composition. Corresponding technical information is usually available from the manufacturers of such additives for this case or can be determined in a simple manner by the person skilled in the art through corresponding preliminary experiments.

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Examples that may be mentioned of light, heat and/or oxidation stabilizers are the following:

alkylated monophenols, such as 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α-methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which have a linear or branched side chain, for example 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1΄-methylundec-1΄-yl)phenol, 2,4-dimethyl-6-(1΄-methyltridec-1΄-yl)phenol and mixtures of these compounds, alkylthiomethylphenols, such as 2,4-dioctylthiomethyl-6-tert-

butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-

30 Hydroquinones and alkylated hydroquinones, such as 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydrocrainone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate and bis(3,5-di-tert-butyl-4-hydroxyphenyl)adipate,

ethylphenol and 2,6-didodecylthiomethyl-4-nonylphenol,

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Tocopherols, such as  $\alpha$ -tocopherol,  $\beta$ -tocopherol,  $\gamma$ -tocopherol,  $\delta$ -tocopherol and mixtures of these compounds, and tocopherol derivatives, such as tocopheryl acetate, succinate, nicotinate and polyoxyethylenesuccinate ("tocofersolate"),

hydroxylated diphenyl thioethers, such as 2,2´-thiobis(6-tert-butyl-4-methylphenol), 2,2´-thiobis(4-octylphenol), 4,4´-thiobis(6-tert-butyl-3-methylphenol), 4,4´-thiobis(6-tert-butyl-2-methylphenol), 4,4´-thiobis(3,6-disec-amylphenol) and 4,4´-bis(2,6-dimethyl-4-hydroxyphenyl)disulfide,

Alkylidenebisphenols, such as 2,2´-methylenebis(6-tert-butyl-4-15 methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'methylenebis[4-methyl-6-(α-methylcyclohexyl)phenol], 2,2´-methylenebis(4methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2-ethylidenebis(4,6-di-tert-20 butylphenol), 2,2´-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2´methylenebis[6-( $\alpha$ -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-( $\alpha$ , $\alpha$ dimethylbenzyl)-4-nonylphenol], 4,4´-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-25 hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-ndodecyl-mercaptobutane, ethylene glycol bis[3,3-bis(3´-tert-butyl-4´-30 hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-

hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3´-tert-butyl-2´-hydroxy-5´-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxy-2-methylphenyl)-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-

- 45 -

PCT/EP2018/053801

n-dodecyl-mercaptobutane and 1,1,5,5-tetrakis(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane,

- O-, N- and S-benzyl compounds, such as 3,5,3′,5′-tetra-tert-butyl-4,4′dihydroxydibenzyl ether, octadecyl 4-hydroxy-3,5dimethylbenzylmercaptoacetate, tridecyl 4-hydroxy-3,5-di-tertbutylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine,
  bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5di-tert-butyl-4-hydroxybenzyl)sulfide and isooctyl-3,5-di-tert-butyl-4hydroxybenzylmercaptoacetate,
- aromatic hydroxybenzyl compounds, such as 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethyl-benzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethyl-benzene and 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol,
- Triazine compounds, such as 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-
- hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate and 1,3,5-tris(2-hydroxyethyl)isocyanurate,
- Benzylphosphonates, such as dimethyl 2,5-di-tert-butyl-4hydroxybenzylphosphonate, diethyl 3,5-di-tert-butyl-4hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-

- 46 -

hydroxybenzylphosphonate and dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate,

- Acylaminophenols, such as 4-hydroxylauroylanilide, 4-hydroxystearoylanilide and octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate,
- Propionic and acetic esters, for example of monohydric or polyhydric

  10 alcohols, such as methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl
  glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol,
  pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-
- bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]-octane,
- Propionamides based on amine derivatives, such as N,N´-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N´-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine and N,N´-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine,
- Ascorbic acid (Vitamin C) and ascorbic acid derivatives, such as ascorbyl palmitate, laurate and stearate, and ascorbyl sulfate and phosphate,
- Antioxidants based on amine compounds, such as N,N´-diisopropyl-pphenylenediamine, N,N´-di-sec-butyl-p-phenylenediamine, N,N´-bis(1,4dimethylpentyl)-p-phenylenediamine, N,N´-bis(1-ethyl-3-methylpentyl)-pphenylenediamine, N,N´-bis(1-methylheptyl)-p-phenylenediamine, N,N´dicyclohexyl-p-phenylenediamine, N,N´-diphenyl-p-phenylenediamine, N,N´
  -bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N´-phenyl-p-

phenylenediamine, N-(1,3-dimethylbutyl)-N´-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N´-phenyl-p-phenylenediamine, N-cyclohexyl-N´phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-5 allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2naphthylamine, octyl-substituted diphenylamine, such as p,p´-di-tertoctyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-10 nonanoylaminophenol, 4-dodecanoylaminophenol, 4octadecanoylaminophenol, bis[4-methoxyphenyl)amine, 2,6-di-tert-butyl-4dimethylaminomethylphenol, 2,4-diaminodiphenylmethane, 4,4'diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-15 diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'dimethylbutyl)phenyl]amine, tert-octyl-substituted N-phenyl-1naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-20 octyldiphenylamine, a mixture of mono- and dialkylated nonyldiphenylamine, a mixture of mono- and dialkylated dodecyldiphenylamine, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamine, a mixture of mono- and dialkylated tert-25 butyldiphenylamine, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tertoctylphenothiazine, a mixture of mono- and dialkylated tertoctylphenothiazine, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperidin-4-30 yl)hexamethylenediamine, bis(2,2,6,6-tetramethylpiperidin-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one and 2,2,6,6-tetramethylpiperidin-4-ol,

Phosphines, Phosphites and phosphonites, such as triphenylphosnine triphenylphosphite, diphenyl alkyl phosphite, phenyl dialkyl phosphite,

tris(nonylphenyl)phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl)phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-

- butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, diisodecyloxy pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl))pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)4,4′-
- biphenylenediphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocine, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocine, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite and bis(2,4-di-tert-butyl-6-methylphenyl)ethyl phosphite,
  - 2-(2´-Hydroxyphenyl)benzotriazoles, such as 2-(2´-hydroxy-5´-methylphenyl)benzotriazole, 2-(3´,5´-di-tert-butyl-2´-
- hydroxyphenyl)benzotriazole, 2-(5´-tert-butyl-2´-hydroxyphenyl)benzotriazole, 2-(2´-hydroxy-5´-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3´,5´-di-tert-butyl-2´-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3´-tert-butyl-2´-hydroxy-5´-
- methylphenyl)-5-chlorobenzotriazole, 2-(3´-sec-butyl-5´-tert-butyl-2´-hydroxyphenyl)benzotriazole, 2-(2´-hydroxy-4´-octyloxyphenyl)benzotriazole, 2-(3´,5´-di-tert-amyl-2´-hydroxyphenyl)benzotriazole, 2-(3,5´-bis-(α,α-dimethylbenzyl)-2´-
- hydroxyphenyl)benzotriazole, a mixture of 2-(3´-tert-butyl-2´-hydroxy-5´-(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3´-tert-butyl-5´-[2-(2-ethylhexyloxy)carbonylethyl]-2´-hydroxy phenyl)-5-chlorobenzotriazole, 2-(3´-tert-butyl-2´-hydroxy-5´-(2-methoxycarbonylethyl)phenyl)-5-
- chlorobenzotriazole, 2-(3´-tert-butyl-2´-hydroxy-5´-(2-

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- 49 -

- methoxycarbonylethyl)phenyl)benzotriazole, 2-(3´-tert-butyl-2´-hydroxy-5´-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3´-tert-butyl-5´-[2-(2-ethylhexyloxy)carbonylethyl]-2´-hydroxy phenyl)benzotriazole, 2-(3´-dodecyl-2´-hydroxy-5´-methylphenyl)benzotriazole and 2-(3´-tert-butyl-2´-hydroxy-5´-(2-isooctyloxycarbonylethyl)phenyl benzotriazole, 2.2´-
- hydroxy-5′-(2-isooctyloxycarbonylethyl)phenyl benzotriazole, 2,2′methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-ylphenol]; the
  product of complete esterification of 2-[3′-tert-butyl-5′-(2-
- methoxycarbonylethyl)-2´-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300;
  - sulfur-containing peroxide scavengers and sulfur-containing antioxidants, such as esters of 3,3´-thiodipropionic acid, for example the lauryl, stearyl, myristyl and tridecyl esters, mercaptobenzimidazole and the zinc salt of 2-mercaptobenzimidazole, dibutylzinc dithiocarbamates, dioctadecyl disulfide and pentaerythritol tetrakis(β-dodecylmercapto)propionate,
- 2-hydroxybenzophenones, such as the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decycloxy, 4-dodecyloxy, 4-benzyloxy, 4,2´,4´-trihydroxy and 2´-hydroxy-4,4´-dimethoxy derivatives,
- Esters of unsubstituted and substituted benzoic acids, such as 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate and 2-methyl-4,6-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate,
- Acrylates, such as ethyl α-cyano- $\beta$ , $\beta$ -diphenylacrylate, isooctyl α-cyano- $\beta$ , $\beta$ -diphenylacrylate, methyl α-methoxycarbonylcinnamate, methyl α-

cyano-β-methyl-p-methoxycinnamate, butyl-α-cyano-β-methyl-pmethoxycinnamate and methyl-α-methoxycarbonyl-p-methoxycinnamate, sterically hindered amines, such as bis(2,2,6,6-tetramethylpiperidin-4yl)sebacate, bis(2,2,6,6-tetramethylpiperidin-4-yl)succinate, bis(1,2,2,6,6pentamethylpiperidin-4-yl)sebacate, bis(1-octyloxy-2,2,6,6tetramethylpiperidin-4-yl)sebacate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl)n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and 10 succinic acid, the condensation product of N,N'-bis(2,2,6,6tetramethylpiperidin-4-yl)hexamethylenediamine and 4-tert-octylamino-2,6dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethylpiperidin-4-yl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethylpiperidin-4-yl)1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethylene)bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-15 tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidin-4-yl)2-n-butyl-2-(2-hydroxy-3,5-di-tertbutylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-20 tetramethylpiperidin-4-yl)sebacate, bis(1-octyloxy-2,2,6,6tetramethylpiperidin-4-yl)succinate, the condensation product of N,N'bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine and 4morpholino-2,6-dichloro-1,3,5-triazine, the condensation product of 2-25 chloro-4.6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidin-4-yl)-1,3,5triazine and 1,2-bis(3-aminopropylamino)ethane, the condensation product of 2-chloro-4.6-di(4-n-butylamino-1.2.2.6.6-pentamethylpiperidin-4-vl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-30 7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethylpiperidin-4-yl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethylpiperidin-4-yl)pyrrolidine-2,5-dione, a mixture of 4hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, the condensation product of N,N'-bis(2,2,6,6-tetramethylpiperidin-4-35 yl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-

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triazine, the condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine, 4-butylamino-2,2,6,6-tetramethylpiperidine, N-(2,2,6,6-tetramethylpiperidin-4-yl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethylpiperidin-4-yl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]-decane, the condensation product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro-[4.5]decane and epichlorohydrin, the condensation products of 4-amino-2,2,6,6-tetramethylpiperidine with tetramethylolacetylenediureas and poly(methoxypropyl-3-oxy)-[4(2,2,6,6-tetramethyl)piperidinyl]-siloxane,

Oxalamides, such as 4,4´-dioctyloxyoxanilide, 2,2´-diethoxyoxanilide, 2,2´
dioctyloxy-5,5´-di-tert-butoxanilide, 2,2´-didodecyloxy-5,5´-di-tertbutoxanilide, 2-ethoxy-2´-ethyloxanilide, N,N´-bis(3dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2´-ethoxanilide and
its mixture with 2-ethoxy-2´-ethyl-5,4´-di-tert-butoxanilide, and mixtures of

ortho-, para-methoxy-disubstituted oxanilides and mixtures of ortho- and
para-ethoxy-disubstituted oxanilides, and

2-(2-hydroxyphenyl)-1,3,5-triazines, such as 2,4,6-tris-(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-4-(2-hydroxy-4-(2-hydroxy-4-(2-hydroxy-4-(2-hydroxy-4-(2-hydroxy-3-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-4-(2-hydroxy-4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-4-(2-hydroxy-4-dimethylphen

dodecyloxypropoxy)phenyl]-4,6-bis-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine and 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

In another preferred embodiment, the polymerisable LC material comprises one or more antioxidant additives, preferably selected from the Irganox® series, e.g. the commercially available antioxidants Irganox®1076 and Irganox®1010, from Ciba, Switzerland.

The polymerizable LC material utilized for the device according to the invention are prepared in a manner conventional per se.

In a preferred embodiment a suitable process for the production of a device according to the present invention, comprises typically the steps of

• providing an electrode structure on the substrate,

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- providing a layer of a polymerisable LC medium comprising one or more multi-, di-, or monoreactive mesogenic compounds onto the substrate or the electrode structure, and
- irradiating the polymerisable LC medium with actinic radiation.

In a preferred embodiment, the polymerisable LC material preferably exhibits a uniform alignment throughout the whole layer.

In a preferred embodiment, the polymerisable LC material exhibits a uniform homeotropic alignment.

In another preferred embodiment, the polymerisable LC material exhibits a uniform planar alignment.

The Friedel-Creagh-Kmetz rule can be used by the skilled person to predict whether a mixture will adopt planar or homeotropic alignment, by comparing the surface energies ( $\gamma$ ) of the RM layer and the substrate or alignment layer:

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If  $\gamma_{RM} > \gamma_s$  the reactive mesogenic compounds will display homeotropic alignment, If  $\gamma_{RM} < \gamma_s$  the reactive mesogenic compounds will display homeotropic alignment.

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When the surface energy of a substrate is relatively low, the intermolecular forces between the reactive mesogens are stronger than the forces across the RM-substrate interface. Therefore, reactive mesogens align perpendicular to the substrate (homeotropic alignment) in order to maximise the intermolecular forces.

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When the surface tension of the substrate is greater than the surface tension of the RMs, the force across the interface dominates. The interface energy is minimised if the reactive mesogens align parallel with the substrate, so the long axis of the RM can interact with the substrate.

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Often the spin-coating itself provides sufficient alignment of the polymerisable LC material.

However, it is likewise possible to provide one or more alignment layers on to the substrate or electrode structure inducing the respective initial alignment of the reactive mesogens (RM) before the polymerisation.

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Suitable alignment layer materials are commonly known to the expert.

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Typical homeotropic alignment layer materials are commonly known to the expert, such as, for example, layers made of alkoxysilanes,

alkyltrichlorosilanes, CTAB, lecithin or polyimides, preferably polyimides, such as, for example JALS-2096-R1 or AL-7511 (Nissan Chemical, Japan).

- 54 -

- Suitable planar alignment layer materials are commonly known to the expert, such as, for example, AL-3046 or AL-1254 both commercially available from JSR.
- In a preferred embodiment, the planar alignment layer is processed by rubbing or photo-alignment techniques known to the skilled person, preferably by rubbing techniques. Accordingly, a uniform preferred direction of the director can be achieved without any physical treatment of the cell like shearing of the cell (mechanical treatment in one direction), etc. The rubbing direction is uncritical and mainly influences only the orientation in which the polarizers have to be applied. Typically the rubbing direction is in the range of +/- 45°, more preferably in the range of +/- 20°, even more preferably, in the range of +/-10, and in particular, in the range of the direction +/- 5° with respect to the substrates largest extension.

Uniform alignment can also be induced or enhanced by additional means like shearing, surface treatment of the substrate, or addition of surfactants to the polymerisable LC material.

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Homeotropic alignment can also be achieved by using amphiphilic materials; they can be added directly to the polymerisable LC material, or the substrate can be treated with these materials in the form of a homeotropic alignment layer. The polar head of the amphiphilic material chemically bonds to the substrate, and the hydrocarbon tail points perpendicular to the substrate. Intermolecular interactions between the amphiphilic material and the RMs promote homeotropic alignment. Commonly used amphiphilic surfactants are known by the expert.

- 55 -

Another method used to promote homeotropic alignment is to apply corona discharge treatment to plastic substrates, generating alcohol or ketone functional groups on the substrate surface. These polar groups can interact with the polar groups present in RMs or surfactants to promote homeotropic alignment.

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In general, reviews of alignment techniques are given for example by I. Sage in "Thermotropic Liquid 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 further review of alignment materials and techniques is given by J. Cognard, Mol. Cryst. Liq. Cryst. 78, Supplement 1 (1981), pages 1-77.

Typically, the alignment layer materials can be applied onto the substrates or electrode structures by conventional coating techniques like spin coating, roll-coating, dip coating, blade coating, doctor-blading, by vapour deposition or conventional printing techniques that are known to the expert, like for example screen printing, offset printing, reel-to-reel printing, letter press printing, gravure printing, rotogravure printing, flexographic printing, intaglio printing, pad printing, heat-seal printing, ink-jet printing or printing by means of a stamp or printing plate.

In a preferred embodiment, the polymerisable LC material is dissolved in a suitable solvent in order to provide a layer of a polymerizable liquid-crystal medium on top of the alignment layer or substrate or electrode structure.

Suitable solvents are preferably selected from organic solvents. The solvents are preferably selected from ketones such as acetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone or cyclohexanone; acetates such as methyl, ethyl or butyl acetate or methyl acetoacetate; alcohols such as methanol, ethanol or isopropyl alcohol;

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aromatic solvents such as toluene or xylene; alicyclic hydrocarbons such as cyclopentane or cyclohexane; halogenated hydrocarbons such as di- or trichloromethane; glycols or their esters such as PGMEA (propyl glycol monomethyl ether acetate),  $\gamma$ -butyrolactone. It is also possible to use binary, ternary or higher mixtures of the above solvents.

- 56 -

In case the polymerisable LC material contains one or more solvents, the total concentration of all solids, including the RMs, in the solvent(s) is preferably from 10 to 60%.

The polymerisable LC medium or a corresponding solution thereof can be applied onto the alignment layer by conventional coating techniques like spin coating, bar coating or blade coating. It can also be applied to the substrate by conventional printing techniques which are known to the expert, like for example screen printing, offset printing, reel-to-reel printing, letter press printing, gravure printing, rotogravure printing, flexographic printing, intaglio printing, pad printing, heat-seal printing, ink-jet printing or printing by means of a stamp or printing plate.

For the production of the polymer films according to the invention, the polymerisable compounds in the polymerisable LC material are polymerised and/or crosslinked by in-situ polymerisation.

The polymerisation can be carried out in one-step. It is also possible to polymerise or crosslink the compounds in a second step, which had not already reacted in the first step ("end curing").

In a preferred method of preparation the polymerisable LC material is coated onto a substrate and subsequently polymerised for example by exposure to heat or actinic radiation as described for example in WO 01/20394, GB 2,315,072 or WO 98/04651.

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- 57 -

PCT/EP2018/053801

Polymerisation of the LC material is preferably achieved by exposing it to 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. In a preferred embodiment, polymerisation is carried out by photo irradiation, in particular with UV light. 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 photo radiation is a laser, like e.g. an UV laser, an IR laser, or a visible laser.

The curing time is dependent, inter alia, on the reactivity of the polymerisable LC material, the thickness of the coated layer, the type of polymerisation initiator and the power of the UV lamp. The curing time is preferably  $\leq 5$  minutes, very preferably  $\leq 3$  minutes, most preferably  $\leq 1$  minute. For mass production, short curing times of  $\leq 30$  seconds are preferred.

A suitable UV radiation power is preferably in the range from approximately 5 mWcm<sup>-2</sup> to approximately 200 mWcm<sup>-2</sup>, more preferably in the range from approximately 50 mWcm<sup>-2</sup> to approximately 175 mWcm<sup>-2</sup> and most preferably in the range from approximately 100 mWcm<sup>-2</sup> to approximately 150 mWcm<sup>-2</sup>.

In connection with the applied UV radiation and as a function of time, a suitable UV dose is preferably in the range from approximately 25 mJcm<sup>-2</sup> to approximately 7500 mJcm<sup>-2</sup> more preferably in the range from approximately 500 mJcm<sup>-2</sup> to approximately 7200 mJcm<sup>-2</sup> and most preferably in the range from approximately 3000 mJcm<sup>-2</sup> to approximately 7000 mJcm<sup>-2</sup>.

Polymerisation is preferably performed under an inert gas atmosphere, preferably in a heated nitrogen atmosphere, but also polymerisation in air is possible.

- Polymerisation is preferably performed at a temperature in the range from from 1°C to 70°C, more preferably 5°C to 50°C, even more preferably 15°C to 30°C.
- In an preferred embodiment, the polymerised film can additionally be post baked at elevated temperature, preferably at above 20°C and below 140°C, more preferably above 40°C and below 130°C and most preferably above 70°C and below 120°C, in order to reach full conversion of the monomers and in order to achieve an optimum stability

Preferably, the resulting liquid crystalline polymer film obtainable or obtained by the process as described above, has a dielectric permittivity in the range from 2.5 to 40, more preferably in the range from 5 to 25.

The permittivity of a material describes how much electric flux is 'generated' per unit charge in that material. More electric flux exists in a material with a high permittivity (per unit charge) because of polarization effects. Permittivity is directly related to electric susceptibility, which is a measure of how easily a dielectric polarizes in response to an electric field. Thus, permittivity relates to a material's ability to transmit (or "permit") an electric field. In SI units, permittivity  $\epsilon$  is measured in farads per meter (F/m); electric susceptibility  $\chi$  is dimensionless. They are related to each other through

$$\varepsilon = \varepsilon_r \, \varepsilon_0 = (1 + \chi) \, \varepsilon_0$$

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where  $\varepsilon_r$  is the relative permittivity of the material, and  $\varepsilon_0 \approx 8.854 \times 10^{-12}$  F/m is the vacuum permittivity.

- For example, the energy from the external electric field stored in the material is characterized by the real part of permittivity ( $\epsilon$ '). The loss factor ( $\epsilon$ '') measures energy dissipation or loss as a material placed in an external electric field.
- In a preferred embodiment, the order parameter of the utilized liquid crystalline polymer film is in the range between 0.4 and 0.9, more preferably 0.5 and 0.7, and most preferably between 0.6 to 0.7.
- The order parameter (S) is defined by the distribution function of the long axes of the monomeric units:

 $S=(3\cos^2\theta -1)2^{-1}$ 

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wherein  $\theta$  is the angle of the long axis of the molecule with the director the value between the brackets average all molecules.

Typically, the order parameter is measured by X-ray diffraction measurement or by dichroic FTIR measurements.

The optical retardation  $(\delta(\lambda))$  of a polymer film as a function of the wavelength of the incident beam  $(\lambda)$  is given by the following equation:  $\delta(\lambda) = (2\pi\Delta n \cdot d)/\lambda$ 

wherein ( $\Delta n$ ) is the birefringence of the film, (d) is the thickness of the film and  $\lambda$  is the wavelength of the incident beam.

According to Snellius law, the birefringence as a function of the direction of the incident beam is defined as

 $\Delta n = \sin\Theta / \sin\Psi$ 

wherein  $\Theta$  is the incidence angle or the tilt angle of the optical axis in the film and  $\Psi$  is the corresponding reflection angle.

Based on these laws, the birefringence and accordingly optical retardation depends on the thickness of an polymer film and the tilt angle of optical axis in the film (cf. Berek's compensator). Therefore, the skilled expert is aware that different optical retardations or different birefringence can be induced by adjusting the orientation of the liquid-crystalline molecules in the polymer film.

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The birefringence ( $\Delta n$ ) of the polymer film according to the present invention is preferably in the range from 0.01 to 0.40, more preferable in the range from 0.01 to 0.25 and even more preferable in the range from 0.01 to 0.16.

The device in accordance with the present invention may furthermore comprise filters which block light of certain wavelengths, for example UV filters. In accordance with the invention, further functional layers, such as, for example, protective films, or heat-insulation films may also be present.

The general functional principle of the device according to the invention will be explained in detail below. It is noted that no restriction of the scope of the claimed invention, which is not present in the claims, is to be derived from the comments on the assumed way of functioning.

In a preferred embodiment, the applied electric field corresponds to a continuous AC field.

Preferably, the applied electric field strength is in the range from 5 V/ $\mu$ m to 70 V/ $\mu$ m.

Without to be bound by the following theory, the formation of the dynamic surface topography or change of the surface shape of the device according to the present invention can be explained by the generation of a free

- 61 -

WO 2018/073459

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PCT/EP2018/053801

volume, where an order parameter reduction and a resonant effect work in concert.

- Without an electric field, the molecules in the polymer network of the utilized polymer film are preferably uniformly aligned and therefore highly ordered and hence, the film is compact.
- When an alternating electric field is applied, dielectric interaction between the field and the reactive mesogens, especially those having a large dipole moment, promotes network vibrations. Subsequently, the rod-like molecular units start to deviate from their initial alignment and nano-voids (molecular voids) are generated also known as dynamic free volume (non-occupied volume).

Preferably, the volume increase due to order parameter reduction is in the range from 1 to 5% more preferably in the range from 2 to 3%.

- When the electrically-induced oscillation frequency coincides with the natural frequency of the polymer film between the electrodes, resonance effects occur which significantly boost the formation of volume.
- 25 Preferably, the frequency of the applied electric field is in the range from larger than 500 Hz to less than 1500 kHz.
  - Consequently, the resonance conditions change upon actuation, which creates a feedback loop that switches resonance on and off. Continuing repeating this cycle forms the loop for the oscillatory topographies until the electric field is stopped.
- Therefore, the present invention relates also to the use of the device according to the present invention, for providing an electro-mechanical effect, which can be sensed by a fingertip or stylus.

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In another preferred embodiment the formation of the dynamic surface topography of the device in accordance with the present invention leads to an electro-optical effect on the incident light, such as, for example, a change from specular to diffuse reflection.

- 62 -

Therefore, in another preferred embodiment, the invention also relates to the use of the device according to the present invention, for providing an electro-optical effect, which can be seen by a change in reflectivity.

The entire device may be fabricated as a thin and lightweight structure that can be attached to electronic devices, such as electro-optic displays, or that can be used as a standalone unit.

Accordingly, the present invention also relates to electro-optical device or electro-mechanical device comprising the device as described above and below, in particular to haptic displays.

The present invention is described above and below with particular reference to the preferred embodiments. It should be understood that various changes and modifications might be made therein without departing from the spirit and scope of the invention.

Many of the compounds or mixtures thereof mentioned above and below are commercially available. All of these compounds are either known or can be prepared by methods which are known per se, as described in the literature (for example in the standard works such as Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for said reactions. Use may also be made here of variants which are known per se, but are not mentioned here.

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PCT/EP2018/053801

It will be appreciated that variations to the foregoing embodiments of the invention can be made while still falling within the scope of the invention. Alternative features serving the same, equivalent, or similar purpose may replace each feature disclosed in this specification, unless stated otherwise. Thus, unless stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

- 63 -

All of the features disclosed in this specification may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. In particular, the preferred features of the invention are applicable to all aspects of the invention and may be used in any combination. Likewise, features described in non-essential combinations may be used separately and not in combination.

It will be appreciated that many of the features described above, particularly of the preferred embodiments, are inventive in their own right and not just as part of an embodiment of the present invention. Independent protection may be sought for these features in addition to or alternative to any invention presently claimed.

The invention will now be described in more detail by reference to the following working examples, which are illustrative only and do not limit the scope of the invention.

The examples below serve to illustrate the invention without limiting it.

## Examples

## Mixture M-1

The following mixture M-1 is prepared.

Compound	%-w/w
$O-(CH_2)_6-O-O$	49.50
O(CH <sub>2</sub> ) <sub>3</sub> O-OO -OOO -OOO -O(CH <sub>2</sub> ) <sub>3</sub> O	24.75
$O(CH_2)_6O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$	24.75
Irgacure®819	1.00

## Example 1

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A glass substrate provided with an array of interdigitated ITO electrodes having an electrode width of 10  $\mu$ m and an electrode gap of 10  $\mu$ m is cleaned by a sequence of a 5 minutes dip in acetone under stirring, 5 minutes dip in propanol-2 under stirring, flushed with demi water followed by drying with a nitrogen flow. AL-7511 (Sunever, Nissan Chemical, Japan) is provided on the substrate by spin coating on the cleaned glass, followed by baking at 200°C for 1 hour. The mixture M-1 is dissolved in dichloromethane in a 20%-w/w concentration. The solution is spin coated on the glass plates with a speed of 1500 rpm, an acceleration of 50 rpm s<sup>-1</sup>, and a duration of 30 seconds. After evaporation of the solvent, the layer stack is irradiated with UV light at room temperature under a N<sub>2</sub>-athmosphere using a mercury lamp (EXPR Omnicure S2000) for 5 minutes. After photopolymerization, the samples are post-baked at 120°C under a N<sub>2</sub>-atmosphere for 10 minutes and cooled down slowly to room temperature (approx. 21°C). The final polymer film thickness is 2.5  $\mu$ m.

The alignment of the polymer film is checked by polarized microscopy (Leica) and the polymer films show a uniform homeotropic alignment.

- 65 -

PCT/EP2018/053801

- Prior to the actuation, a small surface relief with a height of approximately 60 nm is observed, because the polymer film follows the contour of the underneath ITO patterns.
- An alternating electric field with the sine wave function is provided by utilizing a function generator (AFG3252C, Tektronix). The electric signal from the function generator is amplified through an amplifier (F20A, FCL electronics). The output voltage is measured by an oscilloscope (DSOX3032T, Keysight).

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The film polymer film is actuated by an electric field of 75 Volts (equal to 7.5 V/ $\mu$ m) at the frequency of 900 kHz. While applying an AC voltage of 75 V the current in the circuit is measured as 500  $\mu$ A.

Time resolved surface topography is measured using a Digitial Holography Microscope (Lyncee Tech.). The principle of the DHM to form a hologram is to allow two coherent beams (capable of forming interference) with slightly different propagation directions to interfere with each other. The collimated (paralleled) source beam (laser diode), is separated in two beams: the object beam O and the reference beam R. The object beam illuminates the sample via the objective. The retro diffused beam is collected by the objective of the microscope, then recombined with the reference beam to form a hologram in the camera.

The expansion measured between the electrodes reaches up to values of around 6 % of the initial coating thickness. It is calculated as height changes between 'on' and 'off' states over the activated region

- 66 -

(approximately 150 nm) divided by the initial coating thickness of 2.5  $\mu m$  at the same location.

In summary, a new approach in designing a smart coating that can undergo oscillatory dynamics in its surface topographies by addressing an alternating electric field is demonstrated. This new approach is based on (di)electric coupling of polar sub-unites to bring the network into resonance with two orders of dynamics. The first order is the formation of topographies as the external field is switched 'on', which reaches 6 % of the coating thickness. Maintaining the electric field, the topographies start to oscillate both in height and place. Both the field-on and field-off response occur in seconds.

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## **Patent Claims**

- 67 -

- Device comprising at least one substrate provided with an electrode structure and a liquid crystalline polymer film obtainable from a polymerisable LC medium comprising one or more multi-, di- or monoreactive mesogenic compounds, characterized in that the surface shape of said polymer film can be electrically switched.
- 10 2. Device according to claim 1, wherein the substrate is substantially transparent.
  - 3. Device according to claim 1 or 2, wherein the substrate is selected from glass or plastic substrates.
  - 4. Device according to one or more of claims 1 to 3, wherein the electrode structure is selected from an electrode structure, which is capable to allow the application of an electric field, which has at least a substantial component parallel to the substrate main plane or the polymer film.
  - 5. Device according to claim 1 or 4, wherein the electrode structure is an IPS electrode structure.
    - Device according to claim 1 or 5, wherein the multi-, di, or monoreactive mesogenic compounds in the liquid crystalline polymer film are uniformly aligned.
    - 7. Device according to claim 1 or 6, wherein the liquid crystalline polymer film has a dielectric permittivity in the range from 2.5 to 40.
- 8. Device according to claim 1 or 7, wherein the liquid crystalline polymer film has a thickness in the range from 1 to 10 μm.

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- 68 -

PCT/EP2018/053801

- 9. Device according to claim 1 or 8, wherein the liquid crystalline polymer film is obtainable from a polymerisable LC medium comprising one or more direactive mesogenic and optionally one or more monoreactive mesogenic compounds.
- 10. Device according to claim 1 or 9, wherein the liquid crystalline polymer film is obtainable from one or more multi-, di- or monoreactive mesogenic compounds having a dipole moment in the range from 2 to 8 Debye.
- 11. Device according to claim 1 or 10, wherein the applied electric field corresponds to a continuous AC field.
- 12. Device according to claim 1 or 11, wherein the frequency of the applied electric field is in the range from larger than 500 Hz to less than 1500 Hz.
- 13. Device according to claim 1 or 12, wherein the applied electric field strength is in the range from 5 to 70 V/μm.
- 25 14. Process for the production of an device according to one or more of claims 1 to 13, comprising the steps of
  - providing an electrode structure on the substrate
  - providing a layer of a polymerisable LC medium comprising one or more multi-, di-, or monoreactive mesogenic compounds onto the substrate or the electrode structure, and
  - irradiating the polymerisable LC medium with actinic radiation.

- 69 -

PCT/EP2018/053801

15. Use of the device according to one or more of claims 1 to 13, for providing a electromechanical effect, which can be sensed by a fingertip or stylus.

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16. Use of the device according to one or more of claims 1 to 13, for providing a electro optical effect, which can be seen by a change in reflectivity.

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17. Use of the device according to one or more of claims 1 to 13, in an electro-optical device or electro-mechanical device.

18. Electro-optical or electro-mechanical device comprising the device

according to one or more of claims 1 to 13.

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