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(54) Title: LIQUID-CRYSTAL MEDIUM COMPRISING POLYMERIZABLE COMPOUNDS

(57) Abstract: The present invention relates to a polymerizable compound having absorption in the long UV wavelength range, to a liquid-crystal (LC) medium comprising it, and to the use of the compound or LC medium for optical, electro-optical and electronic purposes, in particular in LC displays, especially in LC displays of the PSA (polymer sustained alignment) or SA (self-aligning) mode, to an LC display of the PSA or SA mode comprising the compound or LC medium, and to a process of manufacturing the LC display.

## **Liquid-Crystal Medium Comprising Polymerizable Compounds**

The present invention relates to a polymerizable compound having absorption in the long UV wavelength range, to a liquid-crystal (LC) medium comprising it, and to the use of the compound or LC medium for optical, electro-optical and electronic purposes, in particular in LC displays, especially in LC displays of the PSA (polymer sustained alignment) or SA (self-aligning) mode, to an LC display of the PSA or SA mode comprising the compound or LC medium, and to a process of manufacturing the LC display

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The popularity of 8K and gaming monitors leads to an increased need for LC display (LCD) panels having higher refresh rates and thus for LC media having faster response times. Many of these LCD panels are using polymer stabilized (PS) or polymer sustained alignment modes (PSA) modes, like the PS-VA (vertically aligned), PS-IPS (in-plane switching) or PS-FFS (fringe-field switching) mode or modes derived therefrom, or self-aligned (SA) modes like SA-VA which are polymer stabilized.

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In the PS or PSA mode a small amount, typically from 0.1 to 1% of one or more polymerizable mesogenic compounds, also known as RMs (reactive mesogens), is added to the LC medium. After filling the LC medium into the display the RMs are then polymerized in situ by UV photopolymerization, while a voltage is applied to the electrodes of the display. Thereby a small tilt angle is generated in the LC molecules of the LC medium, which is stabilized by the polymerized RMs. The UV polymerization process, also referred to as "PSA process", is usually carried out in two steps, a first UV exposure step ("UV1 step"), with application of a voltage, to generate the tilt angle, and a second UV exposure step ("UV2 step"), without application of a voltage, to complete polymerization of the RMs.

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In the SA-VA mode the alignment layers are omitted in the display. Instead, a small amount, typically 0.1 to 2.5 %, of a self alignment (SA) additive is added to the LC medium, which induces the desired alignment, for example homeotropic or planar alignment, *in situ* by a self assembling mechanism. The SA additive usually contains an organic, mesogenic core group and attached thereto one or more polar anchor groups, for example hydroxy,

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carboxy, amino or thiol groups, which are capable of interacting with the substrate surface, causing the additives on the substrate surface to align and induce the desired alignment also in the LC molecules. The SA additive may also contain one or more polymerizable groups that can be polymerised under similar conditions as the RMs used in the PSA process. The LC medium may in addition to the SA additive also contain one or more RMs.

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One method to reduce the response times in LC media for the PSA mode is for example by using compounds with an alkenyl group as components of the LC host mixture. However, this may lead to a decrease of the reliability of the mixture when being exposed to the UV light need to polymerize the RMs additives, which is believed to be caused by a reaction of the alkenyl compound with the polyimide of the alignment layer, which is especially problematic when using shorter UV wavelengths of less than 320nm. Therefore there is a tendency to use longer UV wavelengths for the PSA process.

UV-LED lamps have also been proposed for use in the PSA process, as they show less energy consumption, longer lifetime and more effective optical energy transfer to the LC medium due to the narrower emission peak, which allows to reduce the UV intensity and/or UV irradiation time. This enables a reduced tact time and savings in energy and production costs. The UV lamps currently available have higher wavelength emission, for example at 365nm.

Therefore, there is a need for polymerizable LC media which contain RMs that can be effectively polymerized at longer UV wavelengths.

In addition, there is a great demand for PSA or SA displays, and LC media and polymerizable compounds for use in such PSA or SA displays, which enable a high specific resistance at the same time as a large working-temperature range, short response times, even at low temperatures, and a low threshold voltage, a low tilt angle, a high tilt stability, a multiplicity of grey shades, high contrast and a broad viewing angle, have high reliability and high values for the VHR after UV exposure, and, in case of the polymerizable compounds, have low melting points and a high solubility in the LC host

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mixtures. In displays for mobile applications, it is especially desired to have available LC media that show low threshold voltage and high birefringence.

The present invention is based on the object of providing novel suitable
materials, in particular RMs and LC media comprising the same, for use in
PSA or SA displays, which do not have the disadvantages indicated above or
do so to a reduced extent.

In particular, the invention is based on the object of LC media comprising RMs for use in PSA or SA displays, which enable very high specific resistance values, high VHR values, high reliability, low threshold voltages, short response times, high birefringence, show good UV absorption especially at longer UV wavelengths, preferably in the range from 340 to 380 nm, enable quick and complete polymerization of the RMs, allow the generation of a low tilt angle, preferably as quickly as possible, enable a high stability of the tilt angle even after longer time and/or after UV exposure, reduce or prevent the occurrence of "image sticking" and "ODF mura" in the display, and in case of the RMs polymerize as rapidly and completely as possible and show a high solubility in the LC media which are typically used as host mixtures in PSA or SA displays.

A further object of the invention is to provide LC media for use in PSA displays wherein the RMs exhibit both fast polymerization speed and good reliability parameters, like high VHR or tilt stability.

A further object of the invention is the provision of novel LC media containing RMs, in particular for optical, electro-optical and electronic applications, and of suitable processes and intermediates for the preparation thereof.

- A further object of the invention is to provide LC media containing RMs which show one or more of the following advantageous effects:
  - they generate a tilt angle to a desired degree after exposure to UV-light,
- they lead to high tilt stability,

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- they show good UV absorption especially at longer UV wavelengths, especially in the range from 340 to 400 nm, and enable quick and complete polymerization of the RMs at these wavelengths,
- they are suitable for use in PSA displays prepared by a polymerization process using UV-LED lamps,
  - they enable good control of the time range of the first UV-step in which the tilt angle is generated during UV-processing,
  - they enable to keep the time range of the second UV-step, in which any residual RM is polymerized and the tilt angle is stabilized, as short as possible to minimize production cost,
- after the first and second UV-exposure step, the residue RMs have less or no negative effects on the LC-mixture performance parameters, such as VHR, tilt stability, etc.,
- they show good solubility and stability in LC-mixtures in a broad temperature range, preferably from -40 to 140°C.

It was found that one or more of these objects could be achieved by providing polymerizable compounds and LC media comprising them as disclosed and claimed hereinafter.

The invention relates to compounds of formula I

$$R^{a}$$
- $(A^{a}$ - $Z^{a})_{a}$   $(Z^{b}$ - $A^{b})_{b}$ - $R^{b}$ 

wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

R<sup>a</sup>, R<sup>b</sup> P-Sp- or R, wherein at least one of R<sup>a</sup> and R<sup>b</sup> denotes P-Sp-,

	A <sup>a</sup> , A <sup>b</sup>	phenylene-1,4,-diyl or naphthalene,2-6-diyl which is optionally substituted by one or more groups L,
5	$Z^a$ , $Z^b$	-CH=CH-, -CF=CF-, -C≡C- or a single bond, preferably a single bond,
	Р	a polymerizable group,
10	Sp	a spacer group that is optionally substituted by one or more groups P, or a single bond,
	R	straight chain, branched or cyclic alkyl having 1 to 25 C atoms, wherein one or more non-adjacent CH <sub>2</sub> -groups are optionally replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-
15		CO-O-, CR <sup>0</sup> =CR <sup>00</sup> -, -C=C-, or in such a
20		manner that O- and/or S-atoms are not directly connected with each other, and wherein one or more H atoms are each optionally replaced by F or Cl,
	L	F, CI, Br, -CN or straight chain, branched or cyclic alkyl having 1 to 25 C atoms, wherein one or more non-adjacent CH <sub>2</sub> -
25		groups are optionally replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -N(R <sup>0</sup> )-, -Si(R <sup>0</sup> R <sup>00</sup> )-, -CH=CH- or -C≡C- in such a manner that O- and/or S-atoms are not directly connected with each other, and wherein one or more H atoms are each optionally replaced by F or CI,
30	R <sup>0</sup> , R <sup>00</sup>	H or alkyl with 1 to 12 C atoms,
	a, b	0, 1 or 2, preferably 0 or 1,
35	r1	0, 1, 2, 3 or 4, preferably 0, 1 or 2.

The invention further relates to an LC medium comprising one or more polymerizable compounds of formula I.

The invention further relates to an LC medium having negative dielectric
anisotropy and comprising one or more polymerizable compounds of formula
I, preferably showing absorption in the range from 340 to 400 nm, very
preferably from 350 to 380 nm, and further comprising one or more
compounds of formula II

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$$L^{1}$$
 $L^{2}$ 
 $R^{1}$ 
 $(Z^{2}$ 
 $A^{2})_{a2}$ 
 $R^{2}$ 

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wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

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R¹ and R² straight chain, branched or cyclic alkyl having 1 to 25 C atoms, wherein one or more non-adjacent CH₂-groups are optionally replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-,

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O- and/or S-atoms are not directly connected with each other, and wherein one or more H atoms are each optionally replaced by F or CI, preferably alkyl or alkoxy having 1 to 6 C atoms,

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 $\mathsf{R}^0,\,\mathsf{R}^{00}$  H or alkyl with 1 to 12 C atoms, preferably H,

A<sup>1</sup> and A<sup>2</sup> a group selected from the following formulae

preferably from formulae A1, A2, A3, A4, A5, A6, A9 and A10, very preferably from formulae A1, A2, A3, A4, A5, A9 and A10,

 $Z^1$  and  $Z^2$  -CH<sub>2</sub>CH<sub>2</sub>-, -CH=CH-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -CO-O-, -O-CO-, -C<sub>2</sub>F<sub>4</sub>-, -CF=CF-, -CH=CH-CH<sub>2</sub>O- or a single bond, preferably a single bond,

L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup> and L<sup>4</sup> F, CI, OCF<sub>3</sub>, CF<sub>3</sub>, CH<sub>3</sub>, CH<sub>2</sub>F or CHF<sub>2</sub>, preferably F or CI, very preferably F,

Y H, F, Cl, CF<sub>3</sub>, CHF<sub>2</sub> or CH<sub>3</sub>, preferably H or CH<sub>3</sub>, very preferably H,

L<sup>C</sup> CH<sub>3</sub> or OCH<sub>3</sub>, preferably CH<sub>3</sub>,

a1 1 or 2,

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a2 0 or 1.

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The invention further relates to the use of the polymerizable compounds of formula I and the LC media comprising them as described above and below in LC displays of the PSA or SA mode.

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The invention furthermore relates to a process for preparing an LC medium as described above and below, comprising the steps of mixing one or more polymerizable compounds of formula I with one or more compounds of formula II and optionally with further LC compounds and/or additives.

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The invention furthermore relates to an LC display comprising an LC medium according to the invention as described above and below, which is a PSA or SA display, preferably a PS-VA, PS-IPS, PS-FFS or SA-VA display.

The invention furthermore relates to an LC display comprising an LC medium as described above and below wherein the polymerizable compounds are present in polymerized form, which is preferably a PSA or SA display, very preferably a PS-VA, PS-IPS, PS-FFS or SA-VA display.

The invention furthermore relates to an LC display of the PSA type comprising two substrates, at least one which is transparent to light, an electrode provided on each substrate or two electrodes provided on only one of the substrates, and located between the substrates a layer of an LC medium as described above and below, wherein the polymerizable compounds are polymerized between the substrates of the display by UV photopolymerization.

The invention furthermore relates to a process for manufacturing an LC display as described above and below, comprising the steps of filling or otherwise providing an LC medium as described above and below between the substrates of the display, and polymerizing the polymerizable compounds, preferably by irradiation with UV light, preferably having a wavelength >340 nm, preferably >360 nm, preferably in the range from 340 to 400 nm, more preferably in the range from 350 to 390 nm, very preferably in the range from 360 to 380 nm, most preferably in the range from 360 to

368 nm, and preferably while a voltage is applied to the electrodes of the display.

The invention furthermore relates to a process for manufacturing an LC display as described above and below, wherein irradiation of the polymerizable compounds is carried out using a UV-LED lamp.

The LC media according to the present invention show the following advantageous properties when used in PSA displays:

- a suitable tilt generation which is inside a certain process window,
  - fast polymerization leading to minimal residues of RM after the UV-process,
  - a high voltage-holding-ratio after the UV-process,
  - good tilt stability,
  - sufficient stability against heat,
- sufficient solubility in organic solvents typically used in display manufacture.

In addition the LC media according to the present invention help to solve one or more of the following problems:

- to generate a tilt angle to a desired degree after exposure to UV-light,
- to provide a high tilt stability,

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- to show good UV absorption especially at longer UV wavelengths, preferably in the range from 340 to 400 nm, more preferably in the range from 350 to 390 nm, very preferably in the range from 360 to 380 nm, most preferably in the range from 360 to 368 nm, and enable quick and complete polymerization of the RMs at these wavelengths,
- to be suitable for use in PSA displays prepared by a polymerization process using UV-LED lamps,
- to control enable of the time range of the first UV-step in which the tilt angle is generated during UV-processing,
- to keep the time range of the second UV-step as short as possible to minimize production cost,
  - after the first and second UV-exposure step, to reduce or avoid any negative effects of the residual RM on the LC mixture performance parameters, such as VHR, tilt stability, etc.
- to provide good solubility and stability in the LC host mixture in a broad temperature range, preferably from -40°C to ca. 140°C.

An alkenyl group in the compounds of formula II or other components of the LC medium as disclosed below is not considered to be within the meaning of the term "polymerizable group" as used herein. The conditions for the polymerization of the polymerizable compounds of the LC medium are preferably selected such that alkenyl substituents do not participate in the polymerization reaction. Preferably the LC media disclosed and claimed in

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Unless stated otherwise, the polymerizable compounds and the compounds of formula II are preferably selected from achiral compounds.

the present application do not contain an additive that initiates or enhances

the participation of the alkenyl group in a polymerization reaction.

As used herein, the expression "UV light having a wavelength of" followed by a given range of wavelengths (in nm), or by a given lower or upper wavelength limit (in nm), means that the UV emission spectrum of the respective radiation source has an emission peak, which is preferably the highest peak in the respective spectrum, in the given wavelength range or above the given lower wavelength limit or below the given upper wavelength limit and/or that the UV absorption spectrum of the respective chemical compound has a long or short wavelength tail that extends into the given wavelength range or above the given lower wavelength limit or below the given upper wavelength limit.

As used herein, the term "full width half maximum" or "FWHM" means the width of a spectrum curve measured between those points on the *y*-axis which are half the maximum amplitude.

As used herein, the term "substantially transmissive" means that the filter transmits a substantial part, preferably at least 50% of the intensity, of incident light of the desired wavelength(s). As used herein, the term "substantially blocking" means that the filter does not transmit a substantial part, preferably at least 50% of the intensity, of incident light of the undesired wavelengths. As used herein, the term "desired (undesired) wavelength" e.g. in case of a band pass filter means the wavelengths inside (outside) the

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given range of  $\lambda$ , and in case of a cut-off filter means the wavelengths above (below) the given value of  $\lambda$ .

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As used herein, the terms "active layer" and "switchable layer" mean a layer in an electrooptical display, for example an LC display, that comprises one or more molecules having structural and optical anisotropy, like for example LC molecules, which change their orientation upon an external stimulus like an electric or magnetic field, resulting in a change of the transmission of the layer for polarized or unpolarized light.

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As used herein, the terms "tilt" and "tilt angle" will be understood to mean a tilted alignment of the LC molecules of an LC medium relative to the surfaces of the cell in an LC display (here preferably a PSA display), and will be understood to be inclusive of "pretilt" and "pretilt angle". The tilt angle here denotes the average angle (< 90°) between the longitudinal molecular axes of the LC molecules (LC director) and the surface of the plane-parallel outer plates which form the LC cell. A low absolute value for the tilt angle (i.e. a large deviation from the 90° angle) corresponds to a large tilt here. A suitable method for measurement of the tilt angle is given in the examples. Unless indicated otherwise, tilt angle values disclosed above and below relate to this measurement method.

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As used herein, the terms "reactive mesogen" and "RM" will be understood to mean a compound containing a mesogenic or liquid crystalline skeleton, and one or more functional groups attached thereto which are suitable for polymerization and are also referred to as "polymerizable group" or "P".

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Unless stated otherwise, the term "polymerizable compound" as used herein will be understood to mean a polymerizable monomeric compound.

An SA-VA display according to the present invention will be of the polymer

stabilised mode as it contains, or is manufactured by use of, an LC medium containing RMs of formula I and II. Consequently as used herein, the term "SA-VA display" when referring to a display according to the present invention will be understood to refer to a polymer stabilised SA-VA display even if not explicitly mentioned.

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As used herein, the term "low-molecular-weight compound" will be understood to mean to a compound that is monomeric and/or is not prepared by a polymerization reaction, as opposed to a "polymeric compound" or a "polymer".

As used herein, the term "unpolymerizable compound" will be understood to mean a compound that does not contain a functional group that is suitable for polymerization under the conditions usually applied for the polymerization of the RMs.

The term "mesogenic group" as used herein is known to the person skilled in the art and described in the literature, and means a group which, due to the anisotropy of its attracting and repelling interactions, essentially contributes to causing a liquid-crystal (LC) phase in low-molecular-weight or polymeric substances. Compounds containing mesogenic groups (mesogenic compounds) do not necessarily have to have an LC phase themselves. It is also possible for mesogenic compounds to exhibit LC phase behaviour only after mixing with other compounds and/or after polymerization. Typical mesogenic groups are, for example, rigid rod- or disc-shaped units. An overview of the terms and definitions used in connection with mesogenic or LC compounds is given in *Pure Appl. Chem.* 2001, 73(5), 888 and C. Tschierske, G. Pelzl, S. Diele, *Angew. Chem.* 2004, 116, 6340-6368.

The term "spacer group", hereinafter also referred to as "Sp", as used herein is known to the person skilled in the art and is described in the literature, see, for example, *Pure Appl. Chem.* 2001, 73(5), 888 and C. Tschierske, G. Pelzl, S. Diele, *Angew. Chem.* 2004, 116, 6340-6368. As used herein, the terms "spacer group" or "spacer" mean a flexible group, for example an alkylene group, which connects the mesogenic group and the polymerizable group(s) in a polymerizable mesogenic compound.

In a group the single bond shown between the two ring atoms can be attached to any free position of the benzene ring.

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If in the formulae shown above and below a group R<sup>1-13</sup>, R<sup>51</sup>, R<sup>52</sup>, R<sup>Q</sup>, R, R<sup>2A</sup>, R<sup>2B</sup>, R<sup>IIIA</sup>, R<sup>1N</sup>, R<sup>2N</sup>, R<sup>B1</sup>, R<sup>B2</sup>, R<sup>CR1</sup>, R<sup>CR2</sup>, R or L denotes an alkyl radical and/or an alkoxy radical, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6 or 7 C atoms and accordingly preferably denotes ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethoxy, propoxy, butoxy, pentoxy, hexyloxy or heptyloxy, furthermore methyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tridecyloxy or tetradecyloxy.

If in the formulae shown above and below a group R<sup>1-13</sup>, R<sup>51</sup>, R<sup>52</sup>, R<sup>Q</sup>, R, R<sup>2A</sup>, R<sup>2B</sup>, R<sup>IIIA</sup>, R<sup>1N</sup>, R<sup>2N</sup>, R<sup>B1</sup>, R<sup>B2</sup>, R<sup>CR1</sup>, R<sup>CR2</sup>, R or L denotes an alkyl radical wherein one or more CH<sub>2</sub> groups are replaced by S, this may be straight-chain or branched. It is preferably straight-chain, has 1, 2, 3, 4, 5, 6 or 7 C atoms and accordingly preferably denotes thiomethyl, thioethyl, thiopropyl, thiobutyl, thiopentyl, thiohexyl or thioheptyl.

Oxaalkyl preferably denotes straight-chain 2-oxapropyl (= methoxymethyl), 2- (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl.

If in the formulae shown above and below a group R<sup>1-13</sup>, R<sup>51</sup>, R<sup>52</sup>, R<sup>Q</sup>, R, R<sup>2A</sup>, R<sup>2B</sup>, R<sup>IIIA</sup>, R<sup>1N</sup>, R<sup>2N</sup>, R<sup>B1</sup>, R<sup>B2</sup>, R<sup>CR1</sup>, R<sup>CR2</sup>, R or L denotes an alkoxy or oxaalkyl group it may also contain one or more additional oxygen atoms, provided that oxygen atoms are not linked directly to one another.

In another preferred embodiment, one or more of R<sup>1-13</sup>, R<sup>51</sup>, R<sup>52</sup>, R<sup>Q</sup>, R, R<sup>2A</sup>, R<sup>2B</sup>, R<sup>IIIA</sup>, R<sup>1N</sup>, R<sup>2N</sup>, R<sup>B1</sup>, R<sup>B2</sup>, R<sup>CR1</sup>, R<sup>CR2</sup>, R or L are selected from the group

consisting of 
$$S^1$$
  $S^2$ ,  $O_1$   $S^2$ ,  $S^1$   $S^2$ ,  $S^1$   $S^2$ 

If in the formulae shown above and below a group R<sup>1-13</sup>, R<sup>51</sup>, R<sup>52</sup>, R<sup>Q</sup>, R, R<sup>2A</sup>, R<sup>2B</sup>, R<sup>IIIA</sup>, R<sup>1N</sup>, R<sup>2N</sup>, R<sup>B1</sup>, R<sup>B2</sup>, R<sup>CR1</sup>, R<sup>CR2</sup>, R or L denotes an alkyl radical in which one CH<sub>2</sub> group has been replaced by -CH=CH-, this may be straight-chain or branched. It is preferably straight-chain and has 2 to 10 C atoms. Accordingly, it denotes, in particular, vinyl, prop-1- or -2-enyl, but-1-, -2- or -3-enyl, pent-1-, -2-, -3- or -4-enyl, hex-1-, -2-, -3-, -4- or -5-enyl, hept-1-, -2-, -3-, -4-, -5-, -6-, -7- or -8-enyl, dec-1-, -2-, -3-, -4-, -5-, -6-, -7-, -8- or -9-enyl.

If in the formulae shown above and below a group R¹-¹³, R⁵¹, R⁵², R⁰, R, R²A, R²B, R¹IIA, R¹N, R²N, RB¹, RB², RCR¹, RCR², R or L denotes an alkyl or alkenyl radical which is at least monosubstituted by halogen, this radical is preferably straight-chain, and halogen is preferably F or Cl. In the case of polysubstitution, halogen is preferably F. The resultant radicals also include perfluorinated radicals. In the case of monosubstitution, the fluorine or chlorine substituent may be in any desired position, but is preferably in the ω-position.

Halogen is preferably F or CI, very preferably F.

The group -CR<sup>0</sup>=CR<sup>00</sup>- is preferably -CH=CH-.

Preferred substituents L, are, for example, F, Cl, Br, I, -CN, -NO<sub>2</sub>, -NCO, -NCS, -OCN, -SCN, -C(=O)N(R<sup>x</sup>)<sub>2</sub>, -C(=O)Y<sup>1</sup>, -C(=O)R<sup>x</sup>, -N(R<sup>x</sup>)<sub>2</sub>, straight-chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy each having 1 to 25 C atoms, in which one or more H atoms may optionally be replaced by F or Cl, optionally substituted silyl having 1 to 20 Si atoms, or optionally substituted aryl having 6 to 25, preferably 6 to 15, C atoms,

wherein R<sup>x</sup> denotes H, F, CI, CN, or straight chain, branched or cyclic alkyl having 1 to 25 C atoms, wherein one or more non-adjacent CH<sub>2</sub>-groups are optionally replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O- in such a manner that O- and/or S-atoms are not directly connected with each other, and wherein one or more H atoms are each optionally replaced by F, CI, P- or P-Sp-, and

Y<sup>1</sup> denotes halogen.

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Particularly preferred substituents L are, for example, F, Cl, CN, NO<sub>2</sub>, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, COCH<sub>3</sub>, COC<sub>2</sub>H<sub>5</sub>, COOC<sub>4</sub>H<sub>5</sub>, CF<sub>3</sub>, OCF<sub>3</sub>, OCHF<sub>2</sub>, OC<sub>2</sub>F<sub>5</sub>, furthermore phenyl.

in which L has one of the meanings indicated above.

The polymerizable group P is a group which is suitable for a polymerization reaction, such as, for example, free-radical or ionic chain polymerization, polyaddition or polycondensation, or for a polymer-analogous reaction, for

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example addition or condensation onto a main polymer chain. Particular preference is given to groups for chain polymerization, in particular those containing a C=C double bond or -C=C- triple bond, and groups which are suitable for polymerization with ring opening, such as, for example, oxetane or epoxide groups.

Preferred groups P are selected from the group consisting of

CH<sub>2</sub>=CW<sup>1</sup>-CO-O-, CH<sub>2</sub>=CW<sup>1</sup>-CO-, W<sup>2</sup>HC 
$$\stackrel{\bigcirc}{\longrightarrow}$$
 CH-, W<sup>2</sup>  $\stackrel{\bigcirc}{\longrightarrow}$  (CH<sub>2</sub>)<sub>k1</sub>-O-

O,  $CH_2=CW^2-(O)_{k3}-$ ,  $CW^1=CH-CO-(O)_{k3}-$ ,

particular H, F, CI or CH<sub>3</sub>, W<sup>2</sup> and W<sup>3</sup> each, independently of one another, denote H or alkyl having 1 to 5 C atoms, in particular H, methyl, ethyl or n-propyl, W<sup>4</sup>, W<sup>5</sup> and W<sup>6</sup> each, independently of one another, denote CI, oxaalkyl or oxacarbonylalkyl having 1 to 5 C atoms, W<sup>7</sup> and W<sup>8</sup> each, independently of one another, denote H, CI or alkyl having 1 to 5 C atoms, Phe denotes 1,4-phenylene, which is optionally substituted by one or more radicals L as defined above which are other than P-Sp-, k<sub>1</sub>, k<sub>2</sub> and k<sub>3</sub> each.

independently of one another, denote 0 or 1, k<sub>3</sub> preferably denotes 1, and k<sub>4</sub>

denotes an integer from 1 to 10.

Very preferred groups P are selected from the group consisting of

CH<sub>2</sub>=CW<sup>1</sup>-CO-O-, CH<sub>2</sub>=CW<sup>1</sup>-CO-, W<sup>2</sup>HC 
$$\stackrel{\bigcirc}{\longrightarrow}$$
 CH - , W<sup>2</sup>  $\stackrel{\bigcirc}{\longrightarrow}$  (CH<sub>2</sub>)<sub>k1</sub>-O- $\stackrel{\bigcirc}{\longrightarrow}$  W<sup>8</sup> , CH<sub>2</sub>=CW<sup>2</sup>-O-, CH<sub>2</sub>=CW<sup>2</sup>-,

 $CW^1 = CH - CO - (O)_{k3^-}, \ CW^1 = CH - CO - NH -, \ CH_2 = CW^1 - CO - NH -, \ (CH_2 = CH)_2 CH - OCO -, \ (CH_2 = CH - CH_2)_2 CH - OCO -, \ (CH_2 = CH)_2 CH - OCO -, \ (CH_2 = CH - CH_2)_2 N -, \ (CH_2 = CH - CH_2)_2 N - CO -, \ CH_2 = CW^1 - CO - NH -, \ CH_2 = CH - (CO)_{k1} - Phe - (O)_{k2} -, \ CH_2 = CH - (CO)_{k1} - Phe - CH = CH - and \ NATIONAL CONTRACTOR CONTRACTOR$ 

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 $W^4W^5W^6Si$ -, in which  $W^1$  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>,  $W^2$  and  $W^3$  each, independently of one another, denote H or alkyl having 1 to 5 C atoms, in particular H, methyl, ethyl or n-propyl,  $W^4$ ,  $W^5$  and  $W^6$  each, independently of one another, denote Cl, oxaalkyl or oxacarbonylalkyl having 1 to 5 C atoms,  $W^7$  and  $W^6$  each, independently of one another, denote H, Cl or alkyl having 1 to 5 C atoms, Phe denotes 1,4-phenylene,  $k_1$ ,  $k_2$  and  $k_3$  each, independently of one another, denote 0 or 1,  $k_3$  preferably denotes 1, and  $k_4$  denotes an integer from 1 to 10.

Very particularly preferred groups P are selected from the group consisting of CH<sub>2</sub>=CW<sup>1</sup>-CO-O-, in particular CH<sub>2</sub>=CH-CO-O-, CH<sub>2</sub>=C(CH<sub>3</sub>)-CO-O- and CH<sub>2</sub>=CF-CO-O-, furthermore CH<sub>2</sub>=CH-O-, (CH<sub>2</sub>=CH)<sub>2</sub>CH-O-CO-,

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$$(CH_2=CH)_2CH-O-, W^2HC - CH- and W^2 - (CH_2)_{k_1}-O-$$

Further preferred polymerizable groups P are selected from the group consisting of vinyloxy, acrylate, methacrylate, fluoroacrylate, chloroacrylate, oxetane and epoxide, most preferably from acrylate and methacrylate.

Very preferably all polymerizable groups in the polymerizable compound have the same meaning.

If the spacer group Sp is different from a single bond, it is preferably of the formula Sp"-X", so that the respective radical P-Sp- conforms to the formula P-Sp"-X"-, wherein

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denotes linear or branched 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-, -N(R<sup>0</sup>)-, -Si(R<sup>0</sup>R<sup>00</sup>)-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -S-CO-, -CO-S-,  $-N(R^{00})-CO-O-$ ,  $-O-CO-N(R^{0})-$ ,  $-N(R^{0})-CO-N(R^{00})-$ , -CH=CH- or -C=Cin such a way that O and/or S atoms are not linked directly to one another,

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denotes -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CO-N(R0)-, -N(R0)-Χ"  $CO_{-}$ ,  $-N(R^{0})-CO_{-}N(R^{00})-$ ,  $-OCH_{2-}$ ,  $-CH_{2}O_{-}$ ,  $-SCH_{2-}$ ,  $-CH_{2}S_{-}$ ,  $-CF_{2}O_{-}$ , -OCF<sub>2</sub>-, -CF<sub>2</sub>S-, -SCF<sub>2</sub>-, -CF<sub>2</sub>CH<sub>2</sub>-, -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>0</sup>-, -CY<sup>2</sup>=CY<sup>3</sup>-, -C≡C-, -CH=CH-CO-O-, -O-CO-CH=CH- or a single bond,

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each, independently of one another, denote H or alkyl having 1 to 20 C atoms, and

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Y<sup>2</sup> and Y<sup>3</sup> each, independently of one another, denote H, F, Cl or CN.

X" is preferably -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-NR<sup>0</sup>-, -NR<sup>0</sup>-

CO-, -NR<sup>0</sup>-CO-NR<sup>00</sup>- or a single bond.

25 Typical spacer groups Sp and -Sp"-X"- are, for example, -(CH<sub>2</sub>)<sub>p1</sub>-, -(CH<sub>2</sub>)<sub>p1</sub>-O-,  $-(CH_2)_{p_1}-O-CO-$ ,  $-(CH_2)_{p_1}-CO-O-$ ,  $-(CH_2)_{p_1}-O-CO-O-$ ,  $-(CH_2CH_2O)_{q_1}-CH_2CH_2-$ ,  $-(CH_2CH_2O)_{q_1}-CH_2CH_2-$ ,  $-(CH_2CH_2O)_{q_1}-CH_2CH_2 CH_2CH_2-S-CH_2CH_2-$ ,  $-CH_2CH_2-NH-CH_2CH_2-$  or  $-(SiR^0R^{00}-O)_{p1-}$ , in which p1 is an integer from 1 to 12, q1 is an integer from 1 to 3, and R<sup>0</sup> and R<sup>00</sup> have the meanings indicated above.

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Particularly preferred groups Sp and -Sp"-X"- are -(CH<sub>2</sub>)<sub>p1</sub>-, -(CH<sub>2</sub>)<sub>p1</sub>-O-, - $(CH_2)_{p1}$ -O-CO-, - $(CH_2)_{p1}$ -CO-O-, - $(CH_2)_{p1}$ -O-CO-O-, in which p1 and q1 have the meanings indicated above.

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Particularly preferred groups Sp" are, in each case straight-chain, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene,

decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylenethioethylene, ethylene-N-methylimino-ethylene, 1-methylalkylene, ethenylene, propenylene and butenylene.

In a preferred embodiment of the invention the compounds of formula I and its subformulae contain a spacer group Sp that is substituted by one or more polymerizable groups P, so that the group Sp-P corresponds to Sp(P)<sub>s</sub>, with s being ≥2 (branched polymerizable groups).

Preferred compounds of formula I according to this preferred embodiment are those wherein s is 2, i.e. compounds which contain a group Sp(P)<sub>2</sub>. Very preferred compounds of formula I according to this preferred embodiment contain a group selected from the following formulae:

15	-X-alkyl-CHPP	S1
	$-X-alkyl-CH((CH_2)_{aa}P)((CH_2)_{bb}P)\\$	S2
20	$-X-N((CH_2)_{aa}P)((CH_2)_{bb}P)\\$	<b>S</b> 3
20	-X-alkyl-CHP-CH <sub>2</sub> -CH <sub>2</sub> P	S4
	-X-alkyl-C(CH <sub>2</sub> P)(CH <sub>2</sub> P)-C <sub>aa</sub> H <sub>2aa+1</sub>	<b>S</b> 5
25	-X-alkyl-CHP-CH <sub>2</sub> P	S6
	-X-alkyl-CPP-C <sub>aa</sub> H <sub>2aa+1</sub>	<b>S</b> 7
30	-X-alkyl-CHPCHP-C <sub>aa</sub> H <sub>2aa+1</sub>	
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in which P is as defined in formula I,

alkyl denotes a single bond or straight-chain or branched alkylene having
1 to 12 C atoms which is unsubstituted or mono- or polysubstituted
by F, Cl or CN and in which one or more non-adjacent CH<sub>2</sub> groups
may each, independently of one another, be replaced

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by  $-C(R^0)=C(R^0)$ -,  $-C\equiv C$ -,  $-N(R^0)$ -, -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O- in such a way that O and/or S atoms are not linked directly to one another, where  $R^0$  has the meaning indicated above,

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

X has one of the meanings indicated for X", and is preferably O, CO, SO<sub>2</sub>, O-CO-, CO-O or a single bond.

Preferred spacer groups Sp(P)<sub>2</sub> are selected from formulae S1, S2 and S3.

Very peferred spacer groups Sp(P)<sub>2</sub> are selected from the following subformulae:

15	-CHPP	S1a
	-O-CHPP	S1b
20	-CH <sub>2</sub> -CHPP	S1c
20	-OCH <sub>2</sub> -CHPP	S1d
	-CH(CH <sub>2</sub> -P)(CH <sub>2</sub> -P)	S2a
25	$-OCH(CH_2\text{-P})(CH_2\text{-P})$	S2b
	$-CH_2-CH(CH_2-P)(CH_2-P)$	S2c
30	-OCH <sub>2</sub> -CH(CH <sub>2</sub> -P)(CH <sub>2</sub> -P)	S2d
50	$-CO-NH((CH_2)_2P)((CH_2)_2P)$	S3a

P is preferably selected from the group consisting of vinyloxy, acrylate, methacrylate, fluoroacrylate, chloroacrylate, oxetane and epoxide, very preferably from acrylate and methacrylate, most preferably from methacrylate.

Further preferably all polymerizable groups P that are present in the same compound have the same meaning, and very preferably denote acrylate or methacrylate, most preferably methacrylate.

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Sp preferably denotes a single bond or  $-(CH_2)_{p1}$ ,  $-(CH_2)_{p2}$ -CH=CH- $(CH_2)_{p3}$ -,  $-O-(CH_2)_{p1}$ , or  $-CO-O-(CH_2)_{p1}$ , wherein p1 is 2, 3, 4, 5 or 6, preferably 2 or 3, p2 and p3 are independently of each other 0, 1, 2 or 3 and, if Sp is  $-O-(CH_2)_{p1}$ -,  $-O-CO-(CH_2)_{p1}$  or  $-CO-O-(CH_2)_{p1}$  the O-atom or CO-group, respectively, is linked to the benzene ring.

Further preferably at least one group Sp is a single bond.

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Further preferably at least one group Sp is different from a single bond, and is preferably selected from  $-(CH_2)_{p1}$ -,  $-(CH_2)_{p2}$ -CH=CH- $(CH_2)_{p3}$ -,  $-O-(CH_2)_{p1}$ -,  $-O-CO-(CH_2)_{p1}$ , or  $-CO-O-(CH_2)_{p1}$ , wherein p1 is 2, 3, 4, 5 or 6, preferably 2 or 3, p2 and p3 are independently of each other 0, 1, 2 or 3 and, if Sp is  $-O-(CH_2)_{p1}$ -,  $-O-CO-(CH_2)_{p1}$  or  $-CO-O-(CH_2)_{p1}$  the O-atom or CO-group, respectively, is linked to the benzene ring.

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Very preferably Sp is different from a single bond, and is selected from -  $(CH_2)_{2^-}$ , - $(CH_2)_{3^-}$ , - $(CH_2)_{4^-}$ , -O- $(CH_2)_{2^-}$ , -O- $(CH_2)_{3^-}$ , -O-CO- $(CH_2)_{2^-}$  and -CO-O- $(CH_2)_{2^-}$ , wherein the O atom or the CO group is attached to the benzene ring.

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Preferably the polymerizable compounds of formula I have absorption in the range from 340 to 400 nm.

Preferably in the compounds of formula I a and b are independently of each other 0 or 1. In a preferred embodiment of the invention a+b=1 or 2.

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Preferred compounds of formula I are selected from formula I1

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wherein P, Sp, L and r1 have independently of each other one of the meanings given in formula I1 or one of their preferred meanings as given above and below. P is preferably acrylate or methacrylate, very preferably methacrylate. Sp is preferably a single bond. r1 is preferably 0, 1 or 2, very preferably 0 or 1. L is preferably F or OCH<sub>3</sub>. Preferably all groups P in the formulae I and I1 have the same meaning, and very preferably denote methacrylate.

Very preferred compounds of formula I and I1 are selected from the following subformulae.

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Further preferred compounds of formula I and I1 are those selected from one or more of the following embodiments:

- the groups P denote independently of each other acrylate or methacrylate,
   very preferably methacrylate,
  - all groups P in one compound have the same meaning,
  - Sp is a single bond,

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- at least one, preferably one or two of the groups Sp is a single bond and the other groups Sp are different from a single bond,
  - Sp when being different from a single bond, and Sp', are selected from the group consisting of -(CH<sub>2</sub>)<sub>p1</sub>-, -(CH<sub>2</sub>)<sub>p2</sub>-CH=CH-(CH<sub>2</sub>)<sub>p3</sub>-, -O-(CH<sub>2</sub>)<sub>p1</sub>-, -O-CO-(CH<sub>2</sub>)<sub>p1</sub>, wherein p1 is 2, 3, 4, 5 or 6, preferably 2 or 3, p2 and p3 are independently of each other 0, 1, 2 or 3 and, if Sp is -O-(CH<sub>2</sub>)<sub>p1</sub>-, -O-CO-(CH<sub>2</sub>)<sub>p1</sub> or -CO-O-(CH<sub>2</sub>)<sub>p1</sub> the O-atom or CO-group, respectively, is linked to the benzene ring,
  - Sp when being different from a single bond, and Sp', are selected from the the group consisting of -(CH<sub>2</sub>)<sub>2</sub>-, -(CH<sub>2</sub>)<sub>3</sub>-, -(CH<sub>2</sub>)<sub>4</sub>-, -O-(CH<sub>2</sub>)<sub>2</sub>-, -O-(CH<sub>2</sub>)<sub>3</sub>-, -O-CO-(CH<sub>2</sub>)<sub>2</sub> and -CO-O-(CH)<sub>2</sub>-, wherein the O atom or the CO group is attached to the benzene ring,
- L is selected from the group consisting of F, Cl, Br, CN, alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy each having 1 to 6 C atoms or alkenyl having 2 to 6 C atoms, in which one or more H atoms are optionally replaced by F or Cl,

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- L is selected from F, CH<sub>3</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub>, CH=CH<sub>2</sub> and C(CH<sub>3</sub>)=CH<sub>2</sub>, very preferably from F and OCH<sub>3</sub>.

- For use in PSA displays the total proportion of the polymerizable compounds of formula I or its subformulae in the LC medium is preferably from 0.01 to 2.0%, more preferably from 0.1 to 1.0%, very preferably from 0.1 to 0.6%, most preferably from 0.2 to 0.5%.
- For use in SA-VA displays the total proportion of the polymerizable compounds of formula I or its subformulae in the LC medium is preferably from > 0 to < 3%, very preferably from > 0 to < 2%, more preferably from 0.05 to 2.0, most preferably from 0.05 to 1.0%.
- The compounds of the formulae I can be prepared analogously to processes known to the person skilled in the art and described in standard works of organic chemistry, such as, for example, in Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Thieme-Verlag, Stuttgart.
- For example, acrylic or methacrylic esters can be prepared by esterification of the corresponding alcohols with acid derivatives like, for example, (meth)acryloyl chloride or (meth)acrylic anhydride in the presence of a base like pyridine or triethyl amine, and 4-(*N*,*N*-dimethylamino)pyridine (DMAP). Alternatively the esters can be prepared by esterification of the alcohols with (meth)acrylic acid in the presence of a dehydrating reagent, for example according to Steglich with dicyclohexylcarbodiimide (DCC), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide (EDC) or *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride and DMAP.
- The invention furthermore relates to an LC medium or LC display as described above, wherein the polymerizable compounds of formula I1, I2 and optionally I3 are present in polymerized form.
  - The LC display is preferably a PS-VA, PS-IPS, PS-FFS, or SA-VA display.

For the production of PSA or polymer stabilised SA displays, the polymerizable compounds contained in the LC medium are polymerized by in-situ polymerization in the LC medium between the substrates of the LC display, preferably while a voltage is applied to the electrodes.

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The structure of the displays according to the invention corresponds to the usual geometry for PSA displays, as described in the prior art cited at the outset. Geometries without protrusions are preferred, in particular those in which, in addition, the electrode on the colour filter side is unstructured and only the electrode on the TFT side has slots. Particularly suitable and preferred electrode structures for PS-VA displays are described, for example, in US 2006/0066793 A1.

A preferred PSA type LC display of the present invention comprises:

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- a first substrate including a pixel electrode defining pixel areas, the pixel electrode being connected to a switching element disposed in each pixel area and optionally including a micro-slit pattern, and optionally a first alignment layer disposed on the pixel electrode,

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 a second substrate including a common electrode layer, which may be disposed on the entire portion of the second substrate facing the first substrate, and optionally a second alignment layer,

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 an LC layer disposed between the first and second substrates and including an LC medium as described above and below, wherein the polymerizable compounds may also be present in polymerized form.

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The first and/or second alignment layer controls the alignment direction of the LC molecules of the LC layer. For example, in PS-VA displays the alignment layer is selected such that it imparts to the LC molecules homeotropic (or vertical) alignment (i.e. perpendicular to the surface) or tilted alignment. Such an alignment layer may for example comprise a polyimide, which may also be rubbed, or may be prepared by a photoalignment method.

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The LC layer with the LC medium can be deposited between the substrates of the display by methods that are conventionally used by display manufacturers, for example the so-called one-drop-filling (ODF) method. The

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polymerizable component of the LC medium is then polymerized for example by UV photopolymerization. The polymerization can be carried out in one step or in two or more steps.

- The PSA display may comprise further elements, like a colour filter, a black matrix, a passivation layer, optical retardation layers, transistor elements for addressing the individual pixels, etc., all of which are well known to the person skilled in the art and can be employed without inventive skill.
- The electrode structure can be designed by the skilled person depending on the individual display type. For example for PS-VA displays a multi-domain orientation of the LC molecules can be induced by providing electrodes having slits and/or bumps or protrusions in order to create two, four or more different tilt alignment directions.

Upon polymerization the polymerizable compounds form a copolymer, which causes a certain tilt angle of the LC molecules in the LC medium. Without wishing to be bound to a specific theory, it is believed that at least a part of the crosslinked polymer, which is formed by the polymerizable compounds, will phase-separate or precipitate from the LC medium and form a polymer layer on the substrates or electrodes, or the alignment layer provided thereon. Microscopic measurement data (like SEM and AFM) have confirmed that at least a part of the formed polymer accumulates at the LC/substrate interface.

The polymerization can be carried out in one step. It is also possible firstly to carry out the polymerization, optionally while applying a voltage, in a first step in order to produce a tilt angle, and subsequently, in a second polymerization step without an applied voltage, to polymerize or crosslink the compounds which have not reacted in the first step ("end curing").

Suitable and preferred polymerization methods are, for example, thermal or photopolymerization, preferably photopolymerization, in particular UV induced photopolymerization, which can be achieved by exposure of the polymerizable compounds to UV radiation.

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Optionally one or more polymerization initiators are added to the LC medium. Suitable conditions for the polymerization and suitable types and amounts of initiators are known to the person skilled in the art and are described in the literature. Suitable for free-radical polymerization are, for example, the commercially available photoinitiators Irgacure651®, Irgacure184®, Irgacure907®, Irgacure369® or Darocure1173® (Ciba AG). If a polymerization initiator is employed, its proportion is preferably 0.001 to 5% by weight, particularly preferably 0.001 to 1% by weight.

The polymerizable compounds according to the invention are also suitable for polymerization without an initiator, which is accompanied by considerable advantages, such, for example, lower material costs and in particular less contamination of the LC medium by possible residual amounts of the initiator or degradation products thereof. The polymerization can thus also be carried out without the addition of an initiator. In a preferred embodiment, the LC medium thus does not contain a polymerization initiator.

The the LC medium may also comprise one or more stabilisers in order to prevent undesired spontaneous polymerization of the RMs, for example during storage or transport. Suitable types and amounts of stabilisers are known to the person skilled in the art and are described in the literature. Particularly suitable are, for example, the commercially available stabilisers from the Irganox® series (Ciba AG), such as, for example, Irganox® 1076. If stabilisers are employed, their proportion, based on the total amount of RMs or the polymerizable component (component A), is preferably 10-50,000 ppm, particularly preferably 50-5,000 ppm.

In a preferred embodiment the LC media contain one or more chiral dopants, preferably in a concentration from 0.01 to 1% by weight, very preferably from 0.05 to 0.5% by weight. The chiral dopants are preferably selected from the group consisting of compounds from Table B below, very preferably from the group consisting of R- or S-1011, R- or S-2011, R- or S-3011, R- or S-4011, and R- or S-5011.

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In another preferred embodiment the LC media contain a racemate of one or more chiral dopants, which are preferably selected from the chiral dopants mentioned in the previous paragraph.

In another preferred embodiment of the present invention the LC media contain one or more further stabilisers, preferably selected from the the group consisting of the following formulae

$$C_nH_{2n+1} - H O OH$$

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$$C_nH_{2n+1} \longrightarrow O \longrightarrow OH$$
 S2

wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

R<sup>a-d</sup> straight-chain or branched alkyl with 1 to 10, preferably 1 to 6, very preferably 1 to 4 C atoms, most preferably methyl,

X<sup>S</sup> H, CH<sub>3</sub>, OH or O•,

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As straight-chain, branched or cyclic alkylene with 1 to 20 C atoms which is optionally substituted,

n an integer from 1 to 6, preferably 3.

Preferred stabilisers of formula S3 are selected from formulaS3A

wherein n2 is an integer from 1 to 12, and wherein one or more H atoms in the group  $(CH_2)_{n2}$  are optionally replaced by methyl, ethyl, propyl, butyl, pentyl or hexyl.

Very preferred stabilisers are selected from the group consisting of the following formulae

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$$C_3H_7$$
 O OH S2-1

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5 S3-2

10 V

S3-3

20 N

25 S3-4

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In a preferred embodiment the liquid-crystalline medium comprises one or more stabilisers selected from the group consisting of formulae S1-1, S2-1, S3-1, S3-1 and S3-3.

In a preferred embodiment the liquid-crystalline medium comprises one or more stabilisers selected from Table C below.

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Preferably the proportion of stabilisers, like those of formula S1-S3, in the liquid-crystalline medium is from 10 to 500 ppm, very preferably from 20 to 100 ppm.

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In another preferred embodiment the LC medium according to the present invention contains a self alignment (SA) additive, preferably in a concentration of 0.1 to 2.5 %.

In another preferred embodiment the LC medium according to the present invention contains a self alignment (SA) additive, preferably in a concentration of 0.1 to 2.5 %.

In a preferred embodiment the SA-VA display according to the present invention does not contain a polyimide alignment layer. In another preferred embodiment the SA-VA display according to preferred embodiment contains a polyimide alignment layer.

Preferred SA additives for use in this preferred embodiment are selected from compounds comprising a mesogenic group and a straight-chain or branched alkyl side chain that is terminated with one or more polar anchor groups selected from hydroxy, carboxy, amino or thiol groups.

Further preferred SA additives contain one or more polymerizable groups which are attached, optionally via spacer groups, to the mesogenic group. These polymerizable SA additives can be polymerized in the LC medium under similar conditions as applied for the RMs in the PSA process.

Suitable SA additives to induce homeotropic alignment, especially for use in SA-VA mode displays, are disclosed for example in US 2013/0182202 A1, US 2014/0838581 A1, US 2015/0166890 A1 and US 2015/0252265 A1.

In another preferred embodiment an LC medium or a polymer stabilised SA-VA display according to the present invention contains one or more self alignment additives selected from Table E below.

In another preferred embodiment the LC medium according to the present invention contains one or more SA additives, preferably selected from formula II or its subformulae or selected from Table E, in a concentration from 0.1 to 5%, very preferably from 0.2 to 3%, most preferably from 0.2 to 1.5%.

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The polymerizable compounds of formula I1, I2 and I3 do in particular show good UV absorption in, and are therefore especially suitable for, a process of preparing a PSA display including one or more of the following features:

- the polymerizable medium is exposed to UV light in the display in a 2-step process, including a first UV exposure step ("UV1 step"), with application of a voltage, to generate the tilt angle, and a second UV exposure step ("UV2 step"), without application of a voltage, to complete polymerization,
  - the polymerizable medium is exposed to UV light in the display generated by an UV-LED lamp, preferably at least in the UV2 step, more preferably both in the UV1 and UV2 step.
  - the polymerizable medium is exposed to UV light in the display generated by a UV lamp with a radiation spectrum that is shifted to longer wavelengths, preferably ≥340nm, more preferably from 350 to <370 nm, very preferably from 355 to 368 nm, to avoid short UV light exposure in the PS-VA process.

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Both using lower intensity and a UV shift to longer wavelengths protect the organic layer against damage that may be caused by the UV light.

A preferred embodiment of the present invention relates to a process for preparing a PSA display as described above and below, comprising one or more of the following features:

- the polymerizable LC medium is irradiated by UV light in a 2-step process, including a first UV exposure step ("UV1 step"), with application of a voltage, to generate the tilt angle, and a second UV exposure step ("UV2 step"), without application of a voltage, to complete polymerization,
- the polymerizable LC medium is irradiated by UV light generated by a UV lamp having an intensity of from 0.5 mW/cm<sup>2</sup> to 10 mW/cm<sup>2</sup> in the wavelength range from 300-380nm, preferably in the UV2 step, and optionally also in the UV1 step,
- the polymerizable LC medium is irradiated by UV light having a wavelength of ≥340 nm and ≤420 nm, preferably >350 nm, preferably in the range from

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340 to 400 nm, more preferably in the range from 350 to 390 nm, very preferably in the range from 360 to 380 nm, most preferably in the range from 360 to 368 nm.

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- the polymerizable LC medium is irradiated by UV light while a voltage is applied to the electrodes of the display,
- irradiation by UV light is carried out using a UV-LED lamp.

This preferred process can be carried out for example by using the desired UV lamps or by using a band pass filter and/or a cut-off filter, which are substantially transmissive for UV light with the respective desired wavelength(s) and are substantially blocking light with the respective undesired wavelengths. For example, when irradiation with UV light of wavelengths  $\lambda$  of 300-400nm is desired, UV exposure can be carried out using a wide band pass filter being substantially transmissive for wavelengths 300nm <  $\lambda$  < 400nm. When irradiation with UV light of wavelength  $\lambda$  of more than 340 nm is desired, UV irradiation can be carried out using a cut-off filter being substantially transmissive for wavelengths  $\lambda$  > 340 nm.

Preferably UV irradiation is carried out using a UV-LED lamp.

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The use of UV-LED lamps, which have with only one narrow emission peak, in the PSA process proivdes several advantages, like for example a more effective optical energy transfer to the polymerizable compounds in the LC medium, depending on the choice of the suitable polymerizable compounds that shows absorption at the emission wavelength of the LED lamp. This allows to reduce the UV intensity and/or the UV irradiation time, thus enabling a reduced tact time and savings in energy and production costs. Another advantage is that the narrow emission spectrum of the lamp allows an easier selection of the appropriate wavelength for photopolymerization.

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Very preferably the UV light source is an UV-LED lamp emitting a wavelength in the range from 340 to 400 nm, more preferably in the range from 350 to 390 nm, very preferably in the range from 360 to 380 nm, most preferably in the range from 360 to 368 nm. UV-LED lamps emitting UV light with a wavelength of 365 nm are especially preferred.

Preferably the UV-LED lamp emits light having an emission peak with a full width half maximum (FWHM) of 30 nm or less.

- UV-LED lamps are commercially available, for example from Dr. Hoenle AG, Germany or Primelite GmbH, Germany, or IST Metz GmbH, Germany, with emission wavelengths e.g. of 365, 385, 395 and 405 nm.
  - This preferred process enables the manufacture of displays by using longer UV wavelengths, thereby reducing or even avoiding the hazardous and damaging effects of short UV light components.
    - UV radiation energy is in general from 6 to 100 J, depending on the production process conditions.
- The LC medium according to the present invention may additionally comprise one or more further components or additives, preferably selected from the list including but not limited to co-monomers, chiral dopants, polymerization initiators, inhibitors, stabilizers, surfactants, wetting agents, lubricating agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, defoaming agents, deaerators, diluents, reactive diluents, auxiliaries, colourants, dyes, pigments and nanoparticles.
  - The LC medium has preferably a nematic LC phase.

- In another preferred embodiment the LC medium comprises, in addition to the polymerizable compounds of formula I or its subformulae, one or more further polymerizable compounds ("co-monomers"), preferably selected from RMs.
- 30 Suitable and preferred mesogenic comonomers are selected from the following formulae:

$$P^{1}-Sp^{1} \longrightarrow Sp^{2}-P^{2}$$
M1

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$$P^1$$
- $Sp^1$   $Sp^2$ - $P^2$   $M2$ 

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$$P^{1}-Sp^{1} \longrightarrow N \xrightarrow{(L)_{r}} Sp^{2}-P^{2}$$
 M4

$$P^{1}-Sp^{1} \longrightarrow N \xrightarrow{(L)_{r}} Sp^{2}-P^{2}$$

$$P^{1}-Sp^{1} \qquad \qquad N = Sp^{2}-P^{2} \qquad \qquad M6$$

$$P^1-Sp^1$$
  $N$   $Sp^2-P^2$   $M7$ 

25 
$$(L)_r$$
  $(L)_r$   $Sp^2-P^2$  M8

30 
$$P^1-Sp^1$$
  $(L)_s$   $Sp^2-P^2$  M9

$$(L)_{s} \qquad (L)_{t} \qquad (L)_{s} \qquad M10$$

$$35 \qquad P^{1}-Sp^{1} \qquad Sp^{2}-P^{2}$$

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$$P^{1}-Sp^{1}$$
  $Z^{M2}$   $Z^{M3}$   $Z^{M3}$   $Z^{M3}$   $Z^{M2}$   $Z^{M3}$   $Z^{M3}$   $Z^{M3}$   $Z^{M3}$   $Z^{M3}$ 

P<sup>1</sup>-Sp<sup>1</sup> 
$$(L)_r$$
  $(L)_r$   $($ 

$$P^{1}-Sp^{1} \longrightarrow Sp^{2}-P^{2}$$
M14

$$P^{1}-Sp^{1}$$
M15

$$P^{1}-Sp^{1} \longrightarrow O \longrightarrow Sp^{2}-P^{2}$$
 M16

30 
$$P^2-Sp^2$$
  $P^3-Sp^3$  M17

$$P^{2}-Sp^{2}$$
 $P^{3}-Sp^{3}$ 
M18

10 
$$P^{2}-Sp^{2}$$
  $(L)_{r_{r}}$   $Sp^{1}-P^{1}$  M19

15 
$$P^2-Sp^2$$
  $P^3-Sp^3$   $O$   $O$   $M20$ 

$$P^1$$
 $P^2$ 
 $P^3$ 
 $P^2$ 
 $P^3$ 

$$P^{1} \qquad \qquad P^{2} \qquad \qquad M25$$

$$P^{1} \qquad (L)_{r} \qquad (L)_{r} \qquad P^{2} \qquad P^{3}$$

$$P^{1} \xrightarrow{(L)_{r}} \stackrel{(L)_{r}}{\longleftarrow} \stackrel{(L)_{r}}{\longleftarrow} P^{2}$$

$$P^{3}$$

$$P^{1} \xrightarrow{(L)_{r}} P^{2}$$
30

$$P^{1} \xrightarrow{(L)_{r}} P^{2}$$

$$P^{3}$$

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 $R^{aa}$ 

$$P^{1}-Sp^{1} - \left(\begin{matrix} L \end{matrix}\right)_{r} + \left(\begin{matrix} L \end{matrix}\right)_{r}$$

$$P^{1}-Sp^{1} \xrightarrow{(L)_{r}} \stackrel{(L)_{r}}{\downarrow} \stackrel{(L)_{r}}{\downarrow} \stackrel{(L)_{r}}{\downarrow} \stackrel{Sp^{3}-P^{3}}{\downarrow}$$

$$Sp^{2}-P^{2}$$
M31

$$P^1$$
-Sp<sup>1</sup>  $P^2$ -Sp<sup>2</sup>  $P^3$  M32

in which the individual radicals, on each occurrence identically or differently, and each, independently of one another, have the following meaning:

P<sup>1</sup>, P<sup>2</sup>, P<sup>3</sup> a polymerisable group, preferably selected from vinyloxy, acrylate, methacrylate, fluoroacrylate, chloroacrylate, oxetane and epoxy,

Sp<sup>1</sup>, Sp<sup>2</sup>, Sp<sup>3</sup> a single bond or a spacer group where, in addition, one or more of the radicals P<sup>1</sup>-Sp<sup>1</sup>-, P<sup>2</sup>-Sp<sup>2</sup>- and P<sup>3</sup>-Sp<sup>3</sup>- may denote R<sup>aa</sup>, with the proviso that at least one of the radicals P<sup>1</sup>-Sp<sup>1</sup>-, P<sup>2</sup>-Sp<sup>2</sup> and P<sup>3</sup>-Sp<sup>3</sup>- present is different from R<sup>aa</sup>, preferably -(CH<sub>2</sub>)<sub>p1</sub>-, -(CH<sub>2</sub>)<sub>p1</sub>-O-, -(CH<sub>2</sub>)<sub>p1</sub>-CO-O- or -(CH<sub>2</sub>)<sub>p1</sub>-O-CO-O- bedeuten, wherein p1 is an integer from 1 to 12,

H, F, CI, CN or straight-chain or branched alkyl having 1 to 25 C atoms, in which, in addition, one or more non-adjacent  $CH_2$  groups may each be replaced, independently of one another, by  $-C(R^0)=C(R^{00})$ ,  $-C\equiv C$ ,  $-N(R^0)$ , -O, -O, -O, -CO, -O, -O, -O, -O, -O, -O, -O, and in which, in addition, one or more H atoms may be replaced by F, CI, CN

or P¹-Sp¹-, particularly preferably straight-chain or branched, optionally mono- or polyfluorinated alkyl, alkoxy, alkenyl, alkynyl, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having 1 to 12 C atoms (where the alkenyl and alkynyl radicals have at least two C atoms and the branched radicals have at least three C atoms), and wherein Rªa does not denote or contain a group P¹, P² or P³,

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R<sup>0</sup>, R<sup>00</sup> H or alkyl having 1 to 12 C atoms,

R<sup>y</sup> and R<sup>z</sup>

H, F, CH<sub>3</sub> or CF<sub>3</sub>,

 $X^1, X^2, X^3$ 

-CO-O-, -O-CO- or a single bond,

15  $Z^{M1}$ 

 $-O_{-}, -CO_{-}, -C(R^{y}R^{z})_{-} \text{ or } -CF_{2}CF_{2-},$ 

 $Z^{M2}$ .  $Z^{M3}$ 

-CO-O-, -O-CO-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>- or -(CH<sub>2</sub>)<sub>n</sub>-, where n is 2, 3 or 4,

20 L

F, CI, CN or straight-chain or branched, optionally mono- or polyfluorinated alkyl, alkoxy, alkenyl, alkynyl, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having 1 to 12 C atoms,

25 L', L"

H, F or Cl,

k

0 or 1,

r

0, 1, 2, 3 or 4,

30

s

0, 1, 2 or 3,

t

0, 1 or 2,

35

Х

0 or 1.

Very preferred are compounds of formulae M2 and M13, especially direactive compounds containing exactly two polymerizable groups P<sup>1</sup> and P<sup>2</sup>.

Further preferred are compounds selected from formulae M17 to M32, in particular from formulae M20, M22, M24, M27, M30 and M32, especially trireactive compounds containing exactly three polymerizable groups P<sup>1</sup>, P<sup>2</sup> and P<sup>3</sup>.

In the compounds of formulae M1 to M31 the group

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is preferably 
$$\stackrel{L}{\longrightarrow}$$
,  $\stackrel{L}{\longrightarrow}$ ,  $\stackrel{L}{\longrightarrow$ 

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wherein L on each occurrence, identically or differently, has one of the meanings given above or below, and is preferably F, Cl, CN, NO<sub>2</sub>, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C(CH<sub>3</sub>)<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>CH(CH<sub>3</sub>)C<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, COCH<sub>3</sub>, COC<sub>2</sub>H<sub>5</sub>, CF<sub>3</sub>, OCF<sub>3</sub>, OCHF<sub>2</sub>, OC<sub>2</sub>F<sub>5</sub> or P-Sp-, very preferably F, Cl, CN, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, COCH<sub>3</sub>, OCF<sub>3</sub> or P-Sp-, more preferably F, Cl, CH<sub>3</sub>, OCH<sub>3</sub>, COCH<sub>3</sub> or OCF<sub>3</sub>, most preferably F or OCH<sub>3</sub>.

- 25 Preferred compounds of formulae M1 to M32 are those wherein P<sup>1</sup>, P<sup>2</sup> and P<sup>3</sup> denote an acrylate, methacrylate, oxetane or epoxy group, very preferably an acrylate or methacrylate group, most preferably a methacrylate group.
- Further preferred compounds of formulae M1 to M32 are those wherein Sp<sup>1</sup>, Sp<sup>2</sup> and Sp<sup>3</sup> are a single bond.

Further preferred compounds of formulae M1 to M32 are those wherein one of Sp<sup>1</sup>, Sp<sup>2</sup> and Sp<sup>3</sup> is a single bond and another one of Sp<sup>1</sup>, Sp<sup>2</sup> and Sp<sup>3</sup> is different from a single bond.

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Further preferred compounds of formulae M1 to M32 are those wherein those groups  $Sp^1$ ,  $Sp^2$  and  $Sp^3$  that are different from a single bond denote -  $(CH_2)_{s1}$ -X"-, wherein s1 is an integer from 1 to 6, preferably 2, 3, 4 or 5, and X" is X" is the linkage to the benzene ring and is -O-, -O-CO-, -CO-O, or a single bond.

Further preferred compounds of formula M are those selected from Table D below, especially those selected from the group consisting of formulae RM-1, RM-4, RM-8, RM-17, RM-19, RM-35, RM-37, RM-39, RM-40, RM-41, RM-48, RM-52, RM-54, RM-57, RM-64, RM-74, RM-76, RM-88, RM-92, RM-102, RM-103, RM-109, RM-116, RM-117, RM-120, RM-121, RM-122, RM-139, RM-140, RM-142, RM-148, RM-150, RM-151, RM153 and RM-154.

Particularly preferred are LC media comprising one, two or three polymerizable compounds of formula M.

Further preferred are LC media comprising two or more direactive polymerizable compounds of formula M, preferably selected from formulae M1 to M16, very preferably selected from formulae M2 and M13.

Further preferred are LC media comprising one or more direactive polymerizable compounds of formula M, preferably selected from formulae M1 to M16, very preferably from formulae M2 and M13, and one or more trireactive polymerizable compounds of formula M, preferably selected from formulae M17 to M32, very preferably from formulae M20, M22, M24, M27, M30 and M32.

Further preferred are LC media comprising one or more polymerizable compounds of formula M wherein at least one r is not 0, or at least one of s and t is not 0, very preferably selected from formulae M2, M13, M22, M24, M27, M30 and M32, and wherein L is selected from the preferred groups shown above, most preferably from F and OCH<sub>3</sub>.

Further preferred are polymerizable compounds which show absorption in the wavelength range from 320 to 380nm, preferably selected from formula

M, very preferably from formulae M1 to M32, most preferably from the group consisting of the above-mentioned formulae from Table D.

Besides the polymerizable compounds described above, the LC media for use in the LC displays according to the invention comprise an LC mixture ("host mixture") comprising one or more, preferably two or more LC compounds which are selected from low-molecular-weight compounds that are unpolymerizable, and at least one of which is a compound of formula II. These LC compounds are selected such that they stable and/or unreactive to a polymerization reaction under the conditions applied to the polymerization of the polymerizable compounds.

Particularly preferred embodiments of such an LC medium are shown below.

Preferably the LC medium contains one or more compounds of formula II selected from the group consisting of compounds of the formulae IIA, IIB, IIC and IID

$$R^{2A} \xrightarrow{L^1} R^{2B}$$
IIA

$$R^{2A} = Z^2 = Z^{2B} = R^{2B}$$
IIB

$$R^{2A} \xrightarrow{L^3} L^4$$

$$R^{2B}$$
IIC

$$R^{2A}$$
  $Z^{2}$   $Z^{2D}$   $R^{2B}$  IID

in which

R<sup>2A</sup> and R<sup>2B</sup> each, independently of one another, denote H, an alkyl or alkenyl radical having up to 15 C atoms which is unsubstituted, monosubstituted by CN or CF<sub>3</sub> or at least monosubstituted by halogen, where, in addition, one or more CH<sub>2</sub> groups in these radicals may be replaced by -O-, -S-,

radicals may be replaced by -O-, -S-,

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 $-C\equiv C$ -,  $-CF_2O$ -,  $-OCF_2$ -, -OC-O- or -O-CO- in such a way that O atoms are not linked directly to one another,

 $L^1$  to  $L^4$  each, independently of one another, denote F, CI, CF<sub>3</sub> or CHF<sub>2</sub>,

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Y denotes H, F, Cl, CF<sub>3</sub>, CHF<sub>2</sub> or CH<sub>3</sub>, preferably H or CH<sub>3</sub>, particularly preferably H,

25

- Z², Z²B and Z²D each, independently of one another, denote a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH=CH-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -CO O-, -OCO-, -C<sub>2</sub>F<sub>4</sub>-, -CF=CF-, -CH=CHCH<sub>2</sub>O-,
- p denotes 0, 1 or 2, and

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q on each occurrence, identically or differently, denotes 0 or 1.

Preferred compounds of the formulae IIA, IIB, IIC and IID are those wherein  $R^{2B}$  denotes an alkyl or alkoxy radical having up to 15 C atoms, and very preferablydenotes (O)C<sub>v</sub>H<sub>2v+1</sub> wherein (O) is an oxygen atom or a single bond and v is 1, 2, 3, 4, 5 or 6.

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Further preferred compounds of the formulae IIA, IIB, IIC and IID are those wherein R<sup>2A</sup> or R<sup>2B</sup> denotes or contains cycloalkyl or cycloalkoxy radical,

preferably selected from the group consisting of S<sup>1</sup>,

protectably solected from the group consisting of 
$$s^2$$
,  $s^1$   $s^2$ ,  $s^2$ ,  $s^3$ ,  $s^4$ ,  $s^2$ , wherein  $s^4$  is  $c_{1-5-1}$ 

alkylene or  $C_{2-5}$ -alkenylene and  $S^2$  is  $H,\ C_{1-7}$ -alkyl or  $C_{2-7}$ -alkenyl, and very

preferably selected from the group consisting of \_\_\_\_\_, \_\_\_\_,\_\_\_\_

$$C_{2}H_{5}$$
,  $C_{3}H_{7}$ ,  $C_{3}H_{7}$ ,  $C_{3}H_{7}$ ,  $C_{3}H_{4}$ ,  $C_{2}H_{4}$ ,  $C_{3}H_{4}$ ,  $C_{2}H_{4}$ ,  $C_{3}H_{4}$ ,

Further preferred compounds of the formulae IIA, IIB, IIC and IID are indicated below:

alkyl — 
$$CF_2O$$
 —  $O$ -alkyl\* IIA-29

$$-\text{OCF}_2 - \text{O-alkyl*}$$

,

alkyl 
$$CF_2O$$
  $O$  alkyl IIA-38

alkyl
$$+$$
CF<sub>2</sub>O $+$ CF<sub>2</sub>O $+$ CF<sub>2</sub>O $+$ CO)alkyl IIA-39

alkyl—
$$CH_2O$$
— $CH_2O$ 

**IIA-46** 

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$$CF_2O$$
  $CF_2O$   $(O)alkyl^*$  IIB-21

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in which the parameter a denotes 1 or 2, alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms, and alkenyl denotes a straight-chain alkenyl radical having 2-6 C atoms, and (O) denotes an oxygen atom or a single bond. Alkenyl preferably denotes CH<sub>2</sub>=CH-, CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>-, CH<sub>3</sub>-CH=CH-, CH<sub>3</sub>-CH<sub>2</sub>-CH=CH-, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH=CH-, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH=CH- or CH<sub>3</sub>-CH=CH-(CH<sub>2</sub>)<sub>2</sub>-.

Particularly preferred LC media according to the invention comprise one or more compounds of the formulae IIA-2, IIA-8, IIA-10, IIA-16, II-18, IIA-40, IIA-41, IIA-42, IIA-43, IIB-2, IIB-10, IIB-16, IIC-1, and IID-4.

The proportion of compounds of the formulae IIA and/or IIB in the mixture as a whole is preferably at least 20 % by weight.

In another preferred embodiment the LC medium comprises one or more compounds of formula III

in which

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10 R<sup>11</sup> and R<sup>12</sup> each, independently of one another, denote H, an alkyl or alkoxy radical having 1 to 15 C atoms, where one or more CH<sub>2</sub> groups in these radicals may each be replaced, independently

- 20 A<sup>3</sup> on each occurrence, independently of one another, denotes
  - a) 1,4-cyclohexenylene or 1,4-cyclohexylene radical, in which one or two non-adjacent CH<sub>2</sub> groups may be replaced by -O- or -S-,
  - b) a 1,4-phenylene radical, in which one or two CH groups may be replaced by N, or
  - c) a radical selected from the group consisting of spiro[3.3]heptane-2,6-diyl, 1,4-bicyclo[2.2.2]octylene, naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl, 1,2,3,4-tetrahydronaphthalene-2,6-diyl, phenanthrene-2,7-diyl and fluorene-2,7-diyl,

wherein the radicals a), b) and c) may be mono- or polysubstituted by halogen atoms,

n denotes 0, 1 or 2, preferably 0 or 1,

on each occurrence independently of one another denotes -CO-O-, -O-CO-, -CF $_2$ O-, -OCF $_2$ -, -CH $_2$ O-, -OCH $_2$ -, -CH $_2$ -, -CH $_2$ CH $_2$ -, -(CH $_2$ ) $_4$ -, -CH=CH-CH $_2$ O-, -C $_2$ F $_4$ -, -CH $_2$ CF $_2$ -, -CF $_2$ CH $_2$ -, -CF=CF-, -CH=CF-, -CH=CH-, -C\sum C- or a single bond, and

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- 10 L<sup>11</sup> and L<sup>12</sup> each, independently of one another, denote F, Cl, CF<sub>3</sub> or CHF<sub>2</sub>, preferably H or F, most preferably F, and
  - W denotes O or S.

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In a preferred embodiment of the present invention the LC medium comprises one or more compounds of the formula III-1 and/or III-2

$$\begin{array}{c|c}
 & L^{11} & S \\
 & R^{11} & R^{12}
\end{array}$$
III-2

in which the occurring groups have the same meanings as given under formula III above and preferably

- R<sup>11</sup> and R<sup>12</sup> each, independently of one another, an alkyl, alkenyl or alkoxy radical having up to 15 C atoms, more preferably one or both of them denote an alkoxy radical and
  - L<sup>11</sup> and L<sup>12</sup> each preferably denote F.

In another preferred embodiment the LC medium comprises one or more compounds of the formula III-1 selected from the group of compounds of formulae III-1-1 to III-1-11, preferably of formula III-1-6,

5 
$$L^{11}$$
  $O$   $L^{12}$   $alkyl^*$   $III-1-1$ 

10 
$$L^{11}$$
 O  $L^{12}$  alkoxy III-1-2

in which alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms, alkenyl and alkenyl\* each, independently of one another, denote a straight-chain alkenyl radical having 2-6 C atoms, alkoxy and alkoxy\* each, independently of one another, denote a straight-chain alkoxy radical having 1-6 C atoms, and L¹¹ and L¹² each, independently of one another, denote F or CI, preferably both F.

In another preferred embodiment the LC medium comprises one or more compounds of the formula III-2 selected from the group of compounds of formulae III-2-1 to III-2-11, preferably of formula III-2-6,

20 
$$L^{11}$$
  $S$   $L^{12}$   $alkyl^*$   $III-2-1$ 

25 
$$L^{11}$$
 S  $L^{12}$  alkoxy III-2-2

30 
$$alkyl$$
  $S$   $L^{12}$   $alkenyl$  III-2-3

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in which alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms, alkenyl and alkenyl\* each, independently of one another, denote a straight-chain alkenyl radical having 2-6 C atoms, alkoxy and alkoxy\* each, independently of one another, denote a straight-chain alkoxy radical having 1-6 C atoms, and L¹ and L² each, independently of one another, denote F or Cl, preferably both F.

In another preferred embodiment of the present invention the LC medium comprises one or more compounds of the formula IIIA-1 and/or IIIA-2

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$$R^{IIIA}-(O)$$
  $C_nH_{2n}-Cy$  IIIA-1
$$R^{IIIA}-(O)$$
  $C_nH_{2n}-Cy$  IIIA-2

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in which  $L^{11}$  and  $L^{12}$  have the same meanings as given under formula III, (O) denotes O or a single bond,

 $R^{IIIA}$  denotes alkyl or alkenyl having up to 7 C atoms or a group Cy-  $C_mH_{2m+1}$ -,

m and n are, identically or differently, 0, 1, 2, 3, 4, 5 or 6, preferably 1, 2 or 3, very preferably 1, and

Cy denotes a cycloaliphatic group having 3, 4 or 5 ring atoms, which is optionally substituted with alkyl or alkenyl each having up to 3 C atoms, or with halogen or CN, and preferably denotes cyclopropyl, cyclobutyl or cyclopentyl.

The compounds of formula IIIA-1 and/or IIIA-2 are contained in the LC medium either alternatively or additionally to the compounds of formula III, preferably additionally.

Very preferred compounds of the formulae IIIA-1 and IIIA-2 are the following:

in which alkoxy denotes a straight-chain alkoxy radical having 1-6 C atoms.

In a preferred embodiment of the present invention, the LC medium comprises one or more compounds of formula III-3

$$R^{11}$$
  $R^{12}$  III-3

25 in which

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R<sup>11</sup>, R<sup>12</sup> identically or differently, denote H, an alkyl or alkoxy radical having 1 to 15 C atoms, in which one or more CH<sub>2</sub> groups in these radicals are optionally replaced, independently of one another, by

-C=C-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CH=CH-, 
$$\stackrel{,}{\frown}$$
 ,  $\stackrel{,}{\frown}$  ,  $\stackrel{,}{\frown}$  ,  $\stackrel{,}{\frown}$  ,  $\stackrel{,}{\frown}$  , -O-, -CO-O- or -O-CO- in such a way that

O atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by halogen.

III-3-8

The compounds of formula III-3 are preferably selected from the group of compounds of the formulae III-3-1 to III-3-10:

5 
$$R^{12}$$
 III-3-1

10  $R^{12}$  III-3-2

15  $R^{12}$  III-3-2

20  $R^{12}$  III-3-3

21  $R^{13}$  III-3-4

22  $R^{13}$  III-3-5

25  $R^{12}$  III-3-6

30  $R^{12}$  III-3-7

$$F$$
  $S$   $F$   $OR^{12}$  III-3-9

in which R<sup>12</sup> denotes alkyl having 1 to 7 C-atoms, preferably ethyl, n-propyl or n-butyl, or alternatively cyclopropylmethyl, cyclobutylmethyl or cyclopentylmethyl.

In another preferred embodiment of the present invention, the LC medium comprises one or more compounds of the formulae III-4 to III-6, preferably of formula III-5,

$$R^{11}$$
  $R^{12}$  III-4

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$$R^{11}$$
  $R^{12}$  III-5

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$$R^{11}$$
  $R^{12}$  III-6

in which the parameters have the meanings given above, R<sup>11</sup> preferably denotes straight-chain alkyl and R<sup>12</sup> preferably denotes alkoxy, each having 1 to 7 C atoms.

In another preferred embodiment the LC medium comprises one or more compounds of the formula I selected from the group of compounds of formulae III-7 to III-9, preferably of formula III-8,

$$R^{11}$$
  $R^{12}$  III-7

in which the parameters have the meanings given above, R<sup>11</sup> preferably denotes straight-chain alkyl and R<sup>12</sup> preferably denotes alkoxy each having 1 to 7 C atoms.

In a preferred embodiment, the medium comprises one or more compounds of the formula IV,

$$R^{41}$$
  $R^{42}$  IV

in which

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denotes an unsubstituted alkyl radical having 1 to 7 C atoms or an unsubstituted alkenyl radical having 2 to 7 C atoms, preferably an *n*-alkyl radical, particularly preferably having 2, 3, 4 or 5 C atoms, and

R<sup>42</sup> denotes an unsubstituted alkyl radical having 1 to 7 C atoms or an unsubstituted alkoxy radical having 1 to 6 C atoms, both preferably having 2 to 5 C atoms, an unsubstituted alkenyl radical having 2 to 7 C atoms, preferably having 2, 3 or 4 C atoms, more preferably a vinyl radical or a 1-propenyl radical and in particular a vinyl radical.

The compounds of the formula IV are preferably selected from the group of the compounds of the formulae IV-1 to IV-4,

5 alkyl——alkyl' IV-1

10 alkyl——alkenyl

in which

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alkyl and alkyl', independently of one another, denote alkyl having 1 to 7 C atoms, preferably having 2 to 5 C atoms,

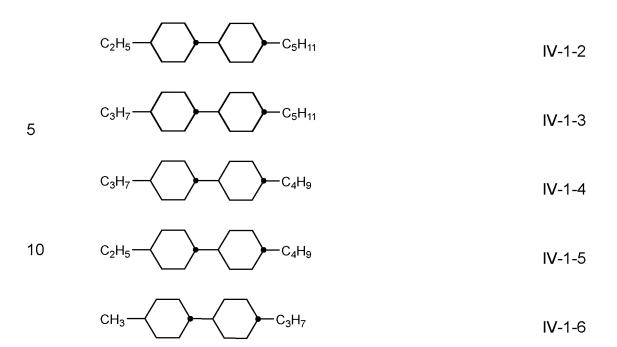
alkenyl denotes an alkenyl radical having 2 to 5 C atoms, preferably having 2 to 4 C atoms, particularly preferably 2 C atoms,

alkenyl' denotes an alkenyl radical having 2 to 5 C atoms, preferably having 2 to 4 C atoms, particularly preferably having 2 to 3 C atoms, and

alkoxy denotes alkoxy having 1 to 5 C atoms, preferably having 2 to 4 C atoms.

Preferably, the LC medium comprises one or more compounds selected from the compounds of the formulae IV-1-1 to IV-1-4

$$C_2H_5$$
  $C_3H_7$  IV-1-1

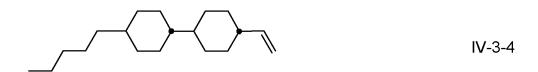


Very preferably, the LC medium according to the invention comprises one or more compounds of the formulae IV-2-1 and/or IV-2-2

$$C_3H_9$$
 OCH<sub>3</sub> IV-1-1

 $C_3H_9$  OC<sub>3</sub>H<sub>9</sub> IV-1-2

Very preferably, the LC medium according to the invention comprises a compound of formula IV-3, in particular selected from the compounds of the formulae IV-3-1 to IV-3-4



Very preferably, the LC medium according to the invention comprises a compound of formula IV-4, in particular selected from the compounds of the formulae IV-4-1 and IV-4-2

The LC medium preferably additionally comprises one or more compounds of the formula IVa,

$$R^{41}$$
  $Z^4$   $A$   $R^{42}$  IVa

in which

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R<sup>41</sup> and R<sup>42</sup> each, independently of one another, denote a straight-chain alkyl, alkoxy, alkenyl, alkoxyalkyl or alkoxy radical having up to 12 C atoms, and

Z<sup>4</sup> denotes a single bond,  $-CH_2CH_2$ -, -CH=CH-,  $-CF_2O$ -,  $-OCF_2$ -,  $-CH_2O$ -,  $-OCH_2$ -, -COO-, -OCO-,  $-C_2F_4$ -,  $-C_4H_8$ - or -CF=CF-.

Preferred compounds of the formula IVa are indicated below:

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in which alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1 to 6 C atoms.

The LC medium according to the invention preferably comprises at least one compound of the formula IVa-1and/or formula IVa-2.

The proportion of compounds of the formula IVa in the mixture as a whole is preferably at least 5 % by weight

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Preferably, the LC medium comprises one or more compounds of formula IVb-1 to IVb-3

in which

alkyl and alkyl\* each, independently of one another, denote a

straight-chain alkyl radical having 1 to 6 C atoms,

and

5 alkenyl and alkenyl\* each, independently of one another, denote a

straight-chain alkenyl radical having 2 to 6 C

atoms.

The proportion of the biphenyls of the formulae IV-1 to IV-3 in the mixture as a whole is preferably at least 3 % by weight, in particular  $\geq$  5 % by weight.

Of the compounds of the formulae IVb-1 to IVb-3, the compounds of the formula IVb-2 are particularly preferred.

15 Particularly preferred biphenyls are

20 IVb-2-1

25 IVb-2-3

in which alkyl\* denotes an alkyl radical having 1 to 6 C atoms and preferably denotes n-propyl.

The LC medium according to the invention particularly preferably comprises one or more compounds of the formulae IVb-1-1 and/or IVb-2-3.

In a preferred embodiment, the LC medium comprises one or more compounds of formula V

5 
$$R^{51}$$
  $Z^{51}$   $A^{51}$   $Z^{52}$   $A^{52}$   $R^{52}$   $V$ 

in which

10 R<sup>51</sup> and R<sup>52</sup> independently of one another, have one of the meanings given for R<sup>41</sup> and R<sup>42</sup> and preferably denote alkyl having 1 to 7 C atoms, preferably n-alkyl, particularly preferably n-alkyl having 1 to 5 C atoms, alkoxy having 1 to 7 C atoms, preferably n-alkoxy, particularly preferably n-alkoxy having 2 to 5 C atoms, alkoxyalkyl, alkenyl or alkenyloxy having 2 to 7 C atoms, preferably having 2 to 4 C atoms, preferably alkenyloxy,

in which

35

 $Z^{51}$ ,  $Z^{52}$  each, independently of one another, denote -CH<sub>2</sub>-CH<sub>2</sub>-, -CH<sub>2</sub>-O-,-CH=CH-, -C $\equiv$ C-, -COO- or a single bond, preferably - CH<sub>2</sub>-CH<sub>2</sub>-, -CH<sub>2</sub>-O- or a single bond and particularly preferably a single bond, and

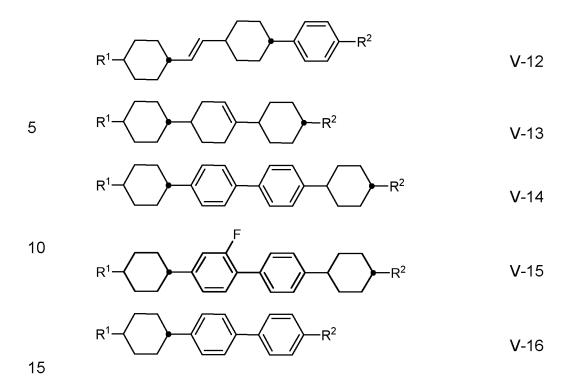
n is 1 or 2.

The compounds of formula V are preferably selected from the compounds of the formulae V-1 to V-16:

5 V-1 V-2 10 V-3 V-4 15 V-5 20 V-6 **V**-7 25 V-8 V-9 30 **V**-10 35 V-11

25

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in which  $R^1$  and  $R^2$  have the meanings indicated for  $R^{2A}$  above.  $R^1$  and  $R^2$  preferably each, independently of one another, denote straight-chain alkyl or alkenyl.

Preferred LC media comprise one or more compounds of the formulae V-1, V-3, V-4, V-6, V-7, V-10, V-11, V-12, V-14, V-15, and/or V-16

LC media according to the invention very particularly preferably comprise the compounds of the formula V-10, V-12, V-16 and/or IV-1, in particular in amounts of 5 to 30 %.

Preferred compounds of the formulae V-10 are indicated below:

$$C_3H_7$$
  $C_3H_7$   $C$ 

The LC medium according to the invention particularly preferably comprises
the tricyclic compounds of the formula V-10a and/or of the formula V-10b in
combination with one or more bicyclic compounds of the formulae IV-1 The
total proportion of the compounds of the formulae V-10a and/or V-10b in
combination with one or more compounds selected from the bicyclohexyl
compounds of the formula IV-1 is 5 to 40 %, very particularly preferably 15 to
35 %.

Very particularly preferred LC media comprise compounds V-10a and CC-2-3

$$C_3H_7$$
  $C_3H_7$   $C_3H_7$   $C_3H_7$   $C_3H_7$   $C_3H_7$   $C_3H_7$   $C_3H_7$ 

25

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The compounds V-10a and IV-1-1 are preferably present in the mixture in a concentration of 15 to 35 %, particularly preferably 15 to 25 % and especially preferably 18 to 22 %, based on the mixture as a whole.

Very particularly preferred LC media comprise the compounds V-10b and IV-1-1:

$$C_3H_7$$
  $C_3H_7$   $V-10b$   $C_2H_5$   $C_3H_7$   $IV-1-1$ .

The compounds V-10b and IV-1-1 are preferably present in the mixture in a concentration of 15 to 35 %, particularly preferably 15 to 25 % and especially preferably 18 to 22 %, based on the mixture as a whole.

Very particularly preferred LC media comprise the following three compounds:

35

$$C_{3}H_{7}$$
 V-10a  $C_{3}H_{7}$  V-10b  $C_{2}H_{5}$   $C_{3}H_{7}$  IV-1-1.

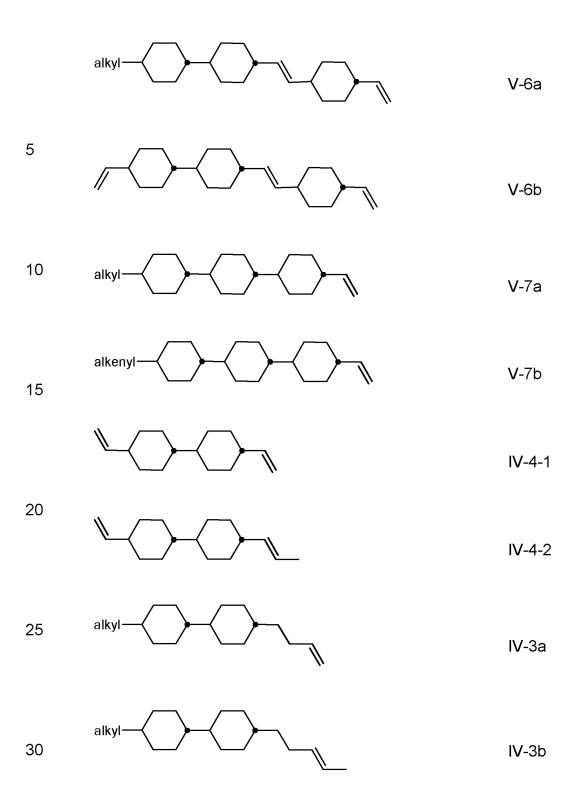
The compounds V-10a, V-10b and IV-1-1 are preferably present in the mixture in a concentration of 15 to 35 %, particularly preferably 15 to 25 % and especially preferably 18 to 22 %, based on the mixture as a whole.

Preferred LC media comprise at least one compound selected from the group of the compounds

$$R^{51}$$
 $R^{52}$ 
 $R^{51}$ 
 $R^{51}$ 
 $R^{52}$ 
 $R^{52}$ 
 $R^{52}$ 
 $R^{41}$ 
 $R^{41}$ 
 $R^{42}$ 
 $R^{42}$ 
 $R^{42}$ 
 $R^{41}$ 

in which  $R^{41}$  and  $R^{42}$ , and  $R^{51}$  and  $R^{52}$  have the meanings indicated above. Preferably in the compounds V-6, V-7 and IV-1,  $R^{41}$  and  $R^{51}$  denotes alkyl or alkenyl having 1 to 6 or 2 to 6 C atoms, respectively, and  $R^{42}$  and  $R^{52}$  denotes alkenyl having 2 to 6 C atoms.

Preferred LC media comprise at least one compound of the formulae V-6a, V-6b, V-7a, V-7b, IV-4-1, IV-4-2, IV-3a and IV-3b:



in which alkyl denotes an alkyl radical having 1 to 6 C atoms and alkenyl denotes an alkenyl radical having 2 to 6 C atoms.

The compounds of the formulae V-6a, V-6b, V-7a, V-7b, IV-4-1, IV-4-2, IV-3a and IV-3b are preferably present in the LC media according to the invention in amounts of 1 to 40 % by weight, preferably 5 to 35 % by weight and very particularly preferably 10 to 30 % by weight.

5

In a preferred embodiment of the present invention the LC medium additionally comprises one or more compounds of the formulae VI-1 to VI-9

10 
$$R^7$$
  $(O)C_wH_{2w+1}$  VI-1

$$R^7$$
  $(O)C_wH_{2w+1}$   $VI-2$ 

$$R^7$$
  $(O)C_wH_{2w+1}$   $VI-3$ 

20

$$R^7$$
  $(O)C_wH_{2w+1}$   $VI-4$ 

VI-5

 $\mathbb{R}^{7} \longrightarrow \mathbb{F} \longrightarrow \mathbb{F}$   $(O)C_{w}H_{2w+1}$ 

30 
$$R^7$$
  $(O)C_wH_{2w+1}$  VI-6

$$R^7$$
  $(O)C_wH_{2w+1}$   $VI-7$ 

$$R^7$$
  $\longrightarrow$   $(O)C_wH_{2w+1}$   $VI-8$ 

$$R^7$$
  $(O)C_wH_{2w+1}$   $VI-9$ 

in which

10

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R<sup>7</sup> each, independently of one another, have one of the meanings indicated for R<sup>2A</sup> in formula IIA, and

w and x each, independently of one another, denote 1 to 6.

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Particular preference is given to LC media comprising at least one compound of the formula V-9.

In a preferred embodiment of the present invention the LC medium additionally comprises one or more compounds of the formulae VII-1 to VII-25,

$$R \longrightarrow F \longrightarrow F$$
 $(O)C_mH_{2m+1}$ 
VII-1

$$R - (O)C_mH_{2m+1}$$
 VII-2

$$R = (O)C_{m}H_{2m+1}$$

$$VII-5$$

$$10 \qquad R = (O)C_{m}H_{2m+1}$$

$$VII-6$$

$$VII-7$$

$$15 \qquad R = (O)C_{m}H_{2m+1}$$

$$VII-8$$

$$20 \qquad R = (O)C_{m}H_{2m+1}$$

$$VII-9$$

$$25 \qquad R = (O)C_{m}H_{2m+1}$$

$$VII-9$$

$$VII-10$$

$$10 \qquad R = (O)C_{m}H_{2m+1}$$

$$VII-11$$

$$10 \qquad R = (O)C_{m}H_{2m+1}$$

$$VII-11$$

$$10 \qquad R = (O)C_{m}H_{2m+1}$$

$$VII-11$$

$$10 \qquad R = (O)C_{m}H_{2m+1}$$

$$11 \qquad VII-11$$

$$11 \qquad VII-12$$

$$R = (O)C_{m}H_{2m+1}$$

$$VII-13$$

$$VII-14$$

$$VII-14$$

$$VII-15$$

$$R = (O)C_{m}H_{2m+1}$$

$$VII-15$$

$$VII-16$$

$$VII-16$$

$$VII-17$$

$$VII-17$$

$$VII-18$$

$$VII-18$$

$$VII-19$$

$$VII-19$$

$$VII-19$$

$$VII-20$$

$$VII-20$$

$$VII-21$$

$$R \longrightarrow K$$
 VII-22

5 
$$R \longrightarrow F \longrightarrow X$$
 VII-23

10 
$$R \longrightarrow X$$
 VII-24

in which

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R denotes a straight-chain alkyl or alkoxy radical having 1 to 6 C atoms, (O) denotes -O- or a single bond, X denotes F, Cl, OCF<sub>3</sub> or OCHF<sub>2</sub>, L<sup>x</sup> denotes H or F, m is 0, 1, 2, 3, 4, 5 or 6 and n is 0, 1, 2, 3 or 4.

R preferably denotes methyl, ethyl, propyl, butyl, pentyl, hexyl, methoxy, ethoxy, propoxy, butoxy, pentoxy.

X preferably denotes F or OCH<sub>3</sub>, very preferably F.

The LC medium according to the invention preferably comprises the terphenyls of the formulae VII-1 to VII-25 in amounts of 2 to 30 % by weight, in particular 5 to 20 % by weight.

Particular preference is given to compounds of the formulae VII-1, VII-2, VII-4, VII-20, VII-21, and VII-22 wherein X denotes F. In these compounds, R preferably denotes alkyl, furthermore alkoxy, each having 1 to 5 C atoms. In the compounds of the formula VII-20, R preferably denotes alkyl or alkenyl, in

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particular alkyl. In the compounds of the formula VII-21, R preferably denotes alkyl. In the compounds of the formulae VII-22 to VII-25, X preferably denotes F.

- The terphenyls of formula VII-1 to VII-25 are preferably employed in the LC media according to the invention if the  $\Delta n$  value of the mixture is to be  $\geq 0.1$ . Preferred LC media comprise 2 to 20 % by weight of one or more terphenyl compounds selected from the group of the compounds of formulae VII-1 to VII-25.
- 10 Further preferred embodiments are listed below:
  - a) LC medium comprising at least one compound of the formulae Z-1 to Z-7,

15 
$$R \longrightarrow F \longrightarrow F$$
 (O)alkyl Z-1

$$R \longrightarrow OCF_2 \longrightarrow OOR_2$$
 Z-3

$$R \longrightarrow OCF_2 \longrightarrow CO)$$
 Z-4

$$R \longrightarrow CF_2O \longrightarrow CF_2O \longrightarrow CO$$
alkyl Z-6

$$R - CH_2O - CH_2 - CO)alkyl Z-7$$

in which R, (O) and alkyl have the meanings indicated above for formula III.

15

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b) Preferred LC media according to the invention comprise one or more substances which contain a tetrahydronaphthyl or naphthyl unit, such as, for example, the compounds of the formulae N-1 to N-5,

$$R^{1N}$$
 $Z^1$ 
 $R^{2N}$ 
 $R^{2N}$ 

$$R^{1N} - Z^{1} - Z^{2} - Z^{2} - R^{2N}$$
 N-3

$$R^{1N} \xrightarrow{\qquad \qquad } Z^2 \xrightarrow{\qquad \qquad } R^{2N}$$

$$R^{1N}$$
 $Z^1$ 
 $R^{2N}$ 
 $R^{2N}$ 

in which R<sup>1N</sup> and R<sup>2N</sup> each, independently of one another, have the meanings indicated for R<sup>2A</sup>, preferably denote straight-chain alkyl, straight-chain alkoxy or straight-chain alkenyl, and

10

Z¹ and Z² each, independently of one another, denote  $-C_2H_4$ -, -CH=CH-,  $-(CH_2)_4$ -,  $-(CH_2)_3O$ -,  $-O(CH_2)_3$ -,  $-CH=CHCH_2CH_2$ -,  $-CH_2CH_2CH=CH$ -,  $-CH_2O$ -,  $-OCH_2$ -, -COO-, -OCO-,  $-C_2F_4$ -, -CF=CF-, -CF=CH-, -CH=CF-,  $-CF_2O$ -,  $-OCF_2$ -,  $-CH_2$ - or a single bond.

15

c) Preferred LC media comprise one or more compounds selected from the group of the difluorodibenzochroman compounds of the formula BC, chromans of the formula CR, and fluorinated phenanthrenes of the formulae PH-1 and PH-2,

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$$\mathbb{R}^{B1}$$
  $\mathbb{R}^{B2}$   $\mathbb{R}^{B2}$ 

25

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$$\mathbb{R}^1$$
  $\mathbb{R}^2$  PH-1

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$$R^1$$
 $R^2$ 
 $R^2$ 
 $R^2$ 

5

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in which

R<sup>B1</sup>, R<sup>B2</sup>, R<sup>CR1</sup>, R<sup>CR2</sup>, R<sup>1</sup>, R<sup>2</sup> each, independently of one another, have the meaning of R<sup>2A</sup>. c is 0, 1 or 2. R<sup>1</sup> and R<sup>2</sup> preferably, independently of one another, denote alkyl or alkoxy having 1 to 6 C atoms.

The LC media according to the invention preferably comprise the compounds of the formulae BC, CR, PH-1, PH-2 in amounts of 3 to 20 % by weight, in particular in amounts of 3 to 15 % by weight.

15

Particularly preferred compounds of the formulae BC and CR are the compounds BC-1 to BC-7 and CR-1 to CR-5,

BC-2

25

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in which

alkyl and alkyl\* each, independently of one another, denote a

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straight-chain alkyl radical having 1 to 6 C atoms,

and

5 alkenyl and

alkenyl\* each, independently of one another, denote a

straight-chain alkenyl radical having 2 to 6 C atoms.

Very particular preference is given to LC media comprising one, two or three compounds of the formula BC-2, BF-1 and/or BF-2.

d) Preferred LC media comprise one or more indane compounds of the formula In,

$$R^{11} + \left( \begin{array}{c} I \\ I \end{array} \right) + \left( \begin{array}{c} I \\ F \end{array} \right) + \left( \begin{array}{c} R^{12} \\ R^{13} \end{array} \right)$$
 In

in which

R<sup>11</sup>, R<sup>12</sup>,

R<sup>13</sup> each, independently of one another, denote a straight-

chain alkyl, alkoxy, alkoxyalkyl or alkenyl radical having 1

to 6 C atoms,

R<sup>12</sup> and R<sup>13</sup> additionally denote halogen, preferably F,

10 i denotes 0, 1 or 2.

20

Preferred compounds of the formula In are the compounds of the formulae In-1 to In-16 indicated below:

30

$$R^{11} \longrightarrow F \qquad In-12$$

Particular preference is given to the compounds of the formulae In-1, In-2, In-3 and In-4.

The compounds of the formula In and the sub-formulae In-1 to In-16 are preferably employed in the LC media according to the invention in

15

20

concentrations ≥ 5 % by weight, in particular 5 to 30 % by weight and very particularly preferably 5 to 25 % by weight.

e) Preferred LC media additionally comprise one or more compounds of the formulae L-1 to L-5,

10 R— (O)-alkyl

 $R^1$   $R^2$  L-4

$$R^1$$
  $R^2$   $L-5$ ,

in which

25

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R and  $R^1$  each, independently of one another, have the meanings indicated for  $R^{2A}$  in formula IIA above, and alkyl denotes an alkyl radical having 1 to 6 C atoms. The parameter s denotes 1 or 2.

The compounds of the formulae L-1 to L-5 are preferably employed in concentrations of 5 to 50 % by weight, in particular 5 to 40 % by weight and very particularly preferably 10 to 40 % by weight.

f) Preferred LC media additionally comprise one or more compounds of formula IIA-Y

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$$R^{11}$$
 $R^{12}$ 
 $R^{12}$ 
IIA-Y

in which  $R^{11}$  and  $R^{12}$  have one of the meanings given for  $R^{2A}$  in formula IIA above, and  $L^1$  and  $L^2$ , identically or differently, denote F or CI.

Preferred compounds of the formula IIA-Y are selected from the group consisting of the following subformulae

10

$$Alkyl \longrightarrow Alkyl^*$$

$$IIA-Y1$$

15

$$Alkyl \longrightarrow Alkoxy \qquad IIA-Y2$$

20

25

30

25

$$\begin{array}{c|c} L^1 & L^2 \\ \hline \\ Alkyl & \hline \\ O\text{-Alkenyl} & IIA-Y7 \end{array}$$

5 
$$L^1$$
  $L^2$  O-Alkenyl IIA-Y8

in which, Alkyl and Alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms, Alkoxy denotes a straight-chain alkoxy radical having 1-6 C atoms, Alkenyl and Alkenyl\* each, independently of one another, denote a straight-chain alkenyl radical having 2-6 C atoms, and O denotes an oxygen atom or a single bond. Alkenyl and Alkenyl\* preferably denote CH<sub>2</sub>=CH-, CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>-, CH<sub>3</sub>-CH=CH-, CH<sub>3</sub>-CH<sub>2</sub>-CH=CH-, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH=CH-, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH=CH- or CH<sub>3</sub>-CH=CH-(CH<sub>2</sub>)<sub>2</sub>-.

Particularly preferred compounds of the formula IIA-Y are selected from the group consisting of following subformulae:

in which Alkoxy and Alkoxy\* have the meanings defined above and preferably denote methoxy, ethoxy, n- propyloxy, n-butyloxy or n-pentyloxy.

5

g) LC medium which additionally comprises one or more quaterphenyl compounds selected from the following formula:

10

$$R^{Q} = \left( \begin{array}{c} L^{Q1} & L^{Q2} & L^{Q3} \\ & L^{Q4} & \\ & L^{Q4} & \end{array} \right)$$

15 wherein

 $R^Q$ 

is alkyl, alkoxy, oxaalkyl or alkoxyalkyl having 1 to 9 C atoms or alkenyl or alkenyloxy having 2 to 9 C atoms, all of which are optionally fluorinated,

20

is F, Cl, halogenated alkyl or alkoxy having 1 to 6 C atoms or halogenated alkenyl or alkenyloxy having 2 to 6 C atoms,

25

 $L^{Q1}$  to  $L^{Q6}$  independently of each other are H or F, with at least one of  $L^{Q1}$  to  $L^{Q6}$  being F.

Preferred compounds of formula Q are those wherein R<sup>Q</sup> denotes straight-chain alkyl with 2 to 6 C-atoms, very preferably ethyl, n-propyl or n-butyl.

30

Preferred compounds of formula Q are those wherein  $L^{Q3}$  and  $L^{Q4}$  are F. Further preferred compounds of formula Q are those wherein  $L^{Q3}$ ,  $L^{Q4}$  and one or two of  $L^{Q1}$  and  $L^{Q2}$  are F.

35

Preferred compounds of formula Q are those wherein  $X^Q$  denotes F or  $OCF_3$ , very preferably F.

The compounds of formula Q are preferably selected from the following subformulae

5

$$R^{Q}$$
  $Q1$ 

10

$$R^Q$$
 $F$ 
 $F$ 
 $F$ 
 $Q_2$ 

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wherein RQ has one of the meanings of formula Q or one of its preferred meanings given above and below, and is preferably ethyl, n-propyl or nbutyl.

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Especially preferred are compounds of formula Q1, in particular those wherein R<sup>Q</sup> is n-propyl.

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Preferably the proportion of compounds of formula Q in the LC host mixture is from >0 to ≤5% by weight, very preferably from 0.05 to 2% by weight, more preferably from 0.1 to 1% by weight, most preferably from 0.1 to 0.8% by weight.

Preferably the LC medium contains 1 to 5, preferably 1 or 2 compounds of formula Q.

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The addition of quaterphenyl compounds of formula Q to the LC host mixture enables to reduce ODF mura, whilst maintaining high UV absorption, enabling quick and complete polymerization, enabling strong and quick tilt angle generation, and increasing the UV stability of the LC medium.

Besides, the addition of compounds of formula Q, which have positive dielectric anisotropy, to the LC medium with negative dielectric anisotropy allows a better control of the values of the dielectric constants  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$ , and in particular enables to achieve a high value of the dielectric constant  $\epsilon_{\parallel}$  while keeping the dielectric anisotropy  $\Delta\epsilon$  constant, thereby reducing the kick-back voltage and reducing image sticking.

The LC media according to the invention preferably comprise

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- one or more compounds of formula I, preferably of formula I1, very preferably selected from formulae I1-1 to I1-10, preferably in a total concentration in the range of from 0.01% to 2.0%, more preferably from 0.1% to 1.0%, most preferably from 0.2% to 0.8%,

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### and/or

- one or more compounds of formula IIA, preferably in a total concentration in the range of from 5% to 30%, more preferably from 7% to 25%, particularly preferably from 10% to 20%;

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#### and/or

- one or more compounds of formulae IIA and IIB, preferably in a total concentration in the range of from 30% to 45%;

# 25 and/or

- one or more compounds of formula IV, preferably in a total concentration in the range of from 35% to 70%, more preferably from 40 % to 65%, particularly preferably from 45% to 60%;

# 30 and/or

- one or more compounds of formula IV-3, preferably in a total concentration in the range of from 35% to 60%, more preferably from 40 % to 55%, particularly preferably from 45% to 50%;

# 35 and/or

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- one or more compounds of formula III-2, preferably of formula III-2-6, preferably in a total concentration in the range of from 2% to 25%, more preferably from 5% to 15%, particularly preferably from 5 to 12%.

- 5 In particular, the medium comprises
  - one or more compounds CY-n-Om, in particular CY-3-O4, CY-5-O4 and/or CY-3-O2, preferably in a total concentration in the range of from 5% to 30%, preferably 10% to 20%;

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# and/or

- one or more compounds PY-n-Om, in particular PY-3-O2 and/or PY-1-O2, preferably in a total concentration in the range of from 5% to 30%, preferably 5% to 20%;

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### and/or

- CPY-n-Om, in particular CPY-2-O2, CPY-3-O2 and/or CPY-5-O2, preferably in concentrations > 5%, in particular 7% to 20%, based on the mixture as a whole,

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### and/or

- one or more compounds CCY-n-Om, preferably CCY-4-O2, CCY-3-O2, CCY-3-O3, CCY-3-O1 and/or CCY-5-O2, preferably in concentrations > 3%, in particular 5 to 15%, based on the mixture as a whole;

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# and/or

one or more compounds CPY-n-Om, preferably CPY-2-O2 and/or CPY-3-O2, preferably in concentrations > 3%, in particular 5 to 15%, based on the mixture as a whole;

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# and/or

- CLY-n-Om, preferably CLY-2-O4, CLY-3-O2 and/or CLY-3-O3, preferably in concentrations > 5%, in particular 10 to 30%, very preferably 15 to 20%, based on the mixture as a whole;

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### and/or

- CPY-n-Om and CY-n-Om, preferably in concentrations of 10 to 80%, based on the mixture as a whole,

### and/or

- CPY-n-Om and PY-n-Om, preferably CPY-2-O2 and/or CPY-3-O2 and PY-3-O2 or PY-1-O2, preferably in concentrations of 5 to 20%, more preferably 10 to 15% to based on the mixture as a whole,

### and/or

 - CC-3-V, preferably in concentrations of 5 to 50%, based on the mixture as a whole.

### and/or

- the compound of the formula CC-3-V1, in a total concentration in the range of from 5 to 40%, more preferably from 15% to 35%, particularly preferably from 20% to 30%,

# and/or

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- one or more compounds of formula B-nO-Om and/or B(S)-nO-Om, in particular the compound B(S)-2O-O4 and/or B(S)-2O-O5, preferably in a concentration in the range of from 2 to 12 %.

# and/or

- 0.1% to 3% of the compound PPGU-3-F.

The invention furthermore relates to an electro-optical display having active-matrix addressing, characterised in that it contains, as dielectric, a liquid-crystalline medium according to claim 1 and wherein the display is a VA, SA-VA, IPS, U-IPS, FFS, UB-FFS, SA-FFS, PS-VA, PS-OCB, PS-IPS, PS-FFS, PS-UB-FFS, PS-posi-VA, PS-TN, polymer stabilised SA-VA or polymer stabilised SA-FFS display.

It is advantageous for the liquid-crystalline medium according to the invention to preferably have a nematic phase from  $\leq$  -20°C to  $\geq$  70°C, particularly

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preferably from  $\leq$  -30°C to  $\geq$  80°C, very particularly preferably from  $\leq$  -40°C to  $\geq$  90°C.

The medium according to the invention has a clearing temperature of 70°C or more, preferably of 74°C or more.

The expression "have a nematic phase" here means on the one hand that no smectic phase and no crystallisation are observed at low temperatures at the corresponding temperature and on the other hand that clearing still does not occur on heating from the nematic phase. The investigation at low temperatures is carried out in a flow viscometer at the corresponding temperature and checked by storage in test cells having a layer thickness corresponding to the electro-optical use for at least 100 hours. If the storage stability at a temperature of -20°C in a corresponding test cell is 1000 h or more, the medium is referred to as stable at this temperature. At temperatures of -30°C and -40°C, the corresponding times are 500 h and 250 h respectively. At high temperatures, the clearing point is measured by conventional methods in capillaries.

The liquid-crystal mixture preferably has a nematic phase range of at least 60 K and a flow viscosity  $v_{20}$  of at most 30 mm<sup>2</sup> · s<sup>-1</sup> at 20°C.

The mixture is nematic at a temperature of -20°C or less, preferably at -30°C or less, very preferably at -40°C or less.

The values of the birefringence  $\Delta n$  in the liquid-crystal mixture are generally between 0.07 and 0.16, preferably between 0.08 and 0.15, very preferably between 0.09 and 0.14.

In a preferred embodiment of the present invention, the medium has a birefringence in the range of from 0.090 to 0.110, preferably from 0.095 to 0.105, in particular from 0.100 to 0.105.

In another preferred embodiment, the medium according to the invention has a birefringence of 0.120 or more, preferably in the range of from 0.125 to 0.145, more preferably from 0.130 to 0.140.

The liquid-crystal mixture according to the invention has a dielectric anisotropy  $\Delta\epsilon$  of -1.5 to -8.0, preferably of -2.0 to - 4.0, in particular -2.5 to -3.5.

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The rotational viscosity  $\gamma_1$  at 20°C is preferably  $\leq$  120 mPa·s, in particular  $\leq$  100 mPa·s.

In a preferred embodiment, the rotational viscosity  $\gamma_1$  at 20°C is  $\leq$  100mPa·s, in particular  $\leq$  95 mPa·s.

The liquid-crystal media according to the invention have relatively low values for the threshold voltage ( $V_0$ ). They are preferably in the range from 1.7 V to 3.0 V, particularly preferably  $\leq$  2.7 V and very particularly preferably  $\leq$  2.5 V.

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For the present invention, the term "threshold voltage" relates to the capacitive threshold  $(V_0)$ , also called the Freedericks threshold, unless explicitly indicated otherwise.

In addition, the liquid-crystal media according to the invention have high values for the voltage holding ratio in liquid-crystal cells.

In general, liquid-crystal media having a low addressing voltage or threshold voltage exhibit a lower voltage holding ratio than those having a higher addressing voltage or threshold voltage and vice versa.

For the present invention, the term "dielectrically positive compounds" denotes compounds having a  $\Delta\epsilon > 1.5$ , the term "dielectrically neutral compounds" denotes those having  $-1.5 \le \Delta\epsilon \le 1.5$  and the term "dielectrically negative compounds" denotes those having  $\Delta\epsilon < -1.5$ . The dielectric anisotropy of the compounds is determined here by dissolving 10 % of the compounds in a liquid-crystalline host and determining the capacitance of the resultant mixture in at least one test cell in each case having a layer thickness of 20 µm with homeotropic and with homogeneous surface alignment at 1 kHz. The measurement voltage is typically 0.5 V to 1.0 V, but is

always lower than the capacitive threshold of the respective liquid-crystal mixture investigated.

All temperature values indicated for the present invention are in °C.

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The LC media according to the invention are suitable for all VA-TFT ( $\underline{v}$ ertical  $\underline{a}$ lignment- $\underline{t}$ hin  $\underline{f}$ ilm  $\underline{t}$ ransistor) applications, such as, for example, VAN ( $\underline{v}$ ertically  $\underline{a}$ ligned  $\underline{n}$ ematic), MVA ( $\underline{m}$ ultidomain VA), (S)-PVA ( $\underline{s}$ uper  $\underline{p}$ atterned VA), ASV ( $\underline{a}$ dvanced  $\underline{s}$ uper  $\underline{v}$ iew, or  $\underline{a}$ xially  $\underline{s}$ ymmetric VA), PSA (polymer sustained VA) and PS-VA ( $\underline{p}$ olymer  $\underline{s}$ tabilized VA). They are furthermore suitable for IPS ( $\underline{i}$ n- $\underline{p}$ lane  $\underline{s}$ witching) and FFS ( $\underline{f}$ ringe  $\underline{f}$ ield  $\underline{s}$ witching) applications having negative  $\Delta \varepsilon$ .

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The nematic LC media in the displays according to the invention generally comprise two components A and B, which themselves consist of one or more individual compounds.

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Component A has significantly negative dielectric anisotropy and gives the nematic phase a dielectric anisotropy of ≤ -0.5. Besides one or more compounds of the formula I, it preferably comprises the compounds of the formulae IIA, IIB and/or IIC, furthermore one or more compounds of the formula IV-1.

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The proportion of component A is preferably between 45 and 100 %, in particular between 60 and 85 %.

For component A, one (or more) individual compound(s) which has (have) a value of  $\Delta\epsilon \le$  -0.8 is (are) preferably selected. This value must be more negative, the smaller the proportion A in the mixture as a whole.

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Component B has pronounced nematogeneity and a flow viscosity of not greater than 30 mm<sup>2</sup> · s<sup>-1</sup>, preferably not greater than 25 mm<sup>2</sup> · s<sup>-1</sup>, at 20°C.

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A multiplicity of suitable materials is known to the person skilled in the art from the literature. Particular preference is given to compounds of the formula O-17.

Particularly preferred individual compounds in component B are extremely low-viscosity nematic liquid crystals having a flow viscosity of not greater than 18 mm<sup>2</sup> · s<sup>-1</sup>, preferably not greater than 12 mm<sup>2</sup> · s<sup>-1</sup>, at 20°C.

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Component B is monotropically or enantiotropically nematic, has no smectic phases and is able to prevent the occurrence of smectic phases down to very low temperatures in LC media. For example, if various materials of high nematogeneity are added to a smectic liquid-crystal mixture, the nematogeneity of these materials can be compared through the degree of suppression of smectic phases that is achieved.

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The mixture may optionally also comprise a component C, comprising compounds having a dielectric anisotropy of  $\Delta\epsilon \ge 1.5$ . These so-called positive compounds are generally present in a mixture of negative dielectric anisotropy in amounts of  $\le 20$  % by weight, based on the mixture as a whole.

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Besides one or more compounds of the formula I1, I2 and optionally I3, the medium preferably comprises 4 to 15, in particular 5 to 12, and particularly preferably < 10, compounds of the formulae IIA, IIB and/or IIC and optionally one or more compounds of the formula IV-1

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Besides compounds of the formula I1, I2 and optionally I3 and the compounds of the formulae IIA, IIB and/or IIC and optionally IV-1, other constituents may also be present, for example in an amount of up to 45 % of the mixture as a whole, but preferably up to 35 %, in particular up to 10 %.

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The other constituents are preferably selected from nematic or nematogenic substances, in particular known substances, from the classes of the azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenyl-cyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-biscyclohexylbiphenyls or cyclohexylpyrimidines, phenyl- or cyclohexyldioxanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolanes and substituted cinnamic acid esters.

The most important compounds which are suitable as constituents of liquidcrystal phases of this type can be characterised by the formula OC

$$R^{20}$$
-L-G-E- $R^{21}$  OC

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in which L and E each denote a carbo- or heterocyclic ring system from the group formed by 1,4-disubstituted benzene and cyclohexane rings, 4,4'-disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, di- and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline,

	G denotes	-CH=CH-	-N(O)=N-
		-CH=CQ-	-CH=N(O)-
15		-C≡C-	-CH <sub>2</sub> -CH <sub>2</sub> -
		-CO-O-	-CH <sub>2</sub> -O-
		-CO-S-	-CH <sub>2</sub> -S-
		-CH=N-	-COO-Phe-COO-
20		-CF <sub>2</sub> O-	-CF=CF-
		-OCF <sub>2</sub> -	-OCH <sub>2</sub> -
		-(CH <sub>2</sub> ) <sub>4</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> O-

or a C-C single bond, Q denotes halogen, preferably chlorine, or -CN, and R<sup>20</sup> and R<sup>21</sup> each denote alkyl, alkenyl, alkoxy, alkoxyalkyl or alkoxycarbonyloxy having up to 18, preferably up to 8, carbon atoms, or one of these radicals alternatively denotes CN, NC, NO<sub>2</sub>, NCS, CF<sub>3</sub>, SF<sub>5</sub>, OCF<sub>3</sub>, F, Cl or Br.

In most of these compounds, R<sup>20</sup> and R<sup>21</sup> are different from one another, one of these radicals usually being an alkyl or alkoxy group. Other variants of the proposed substituents are also common. Many such substances or also mixtures thereof are commercially available. All these substances can be prepared by methods known from the literature.

It goes without saying for the person skilled in the art that the VA, IPS or FFS mixture according to the invention may also comprise compounds in which,

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for example, H, N, O, Cl and F have been replaced by the corresponding isotopes.

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The combination of compounds of the preferred embodiments mentioned
above with the polymerized compounds described above causes low
threshold voltages, low rotational viscosities and very good low-temperature
stabilities in the LC media according to the invention at the same time as
constantly high clearing points and high HR values, and allows the rapid
establishment of a particularly low tilt angle (i.e. a large tilt) in PSA displays.

In particular, the LC media exhibit significantly shortened response times, in
particular also the grey-shade response times, in PSA displays compared
with the LC media from the prior art.

The LC media according to the invention may also comprise further additives
which are known to the person skilled in the art and are described in the
literature, such as, for example, polymerization initiators, inhibitors,
stabilisers, surface-active substances or chiral dopants. These may be
polymerizable or non-polymerizable. Polymerizable additives are accordingly
ascribed to the polymerizable component or component A). Nonpolymerizable additives are accordingly ascribed to the non-polymerizable
component or component B).

Furthermore, it is possible to add to the LC media, for example, 0 to 15% by weight of pleochroic dyes, furthermore nanoparticles, conductive salts, preferably ethyldimethyldodecylammonium 4-hexoxybenzoate, tetrabutyl-ammonium tetraphenylborate or complex salts of crown ethers (cf., for example, Haller et al., Mol. Cryst. Liq. Cryst. 24, 249-258 (1973)), for improving the conductivity, or substances for modifying the dielectric anisotropy, the viscosity and/or the alignment of the nematic phases. Substances of this type are described, for example, in DE-A 22 09 127, 22 40 864, 23 21 632, 23 38 281, 24 50 088, 26 37 430 and 28 53 728.

The individual components of the above-listed preferred embodiments of the LC media according to the invention are either known or methods for the preparation thereof can readily be derived from the prior art by the person skilled in the relevant art, since they are based on standard methods

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described in the literature. Corresponding compounds of the formula CY are described, for example, in EP-A-0 364 538. Corresponding compounds of the formula ZK are described, for example, in DE-A-26 36 684 and DE-A-33 21 373.

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The LC media which can be used in accordance with the invention are prepared in a manner conventional per se, for example by mixing one or more of the above-mentioned compounds with one or more polymerizable compounds as defined above, and optionally with further liquid-crystalline compounds and/or additives. In general, the desired amount of the components used in lesser amount is dissolved in the components making up the principal constituent, advantageously at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, for example by distillation, after thorough mixing. The invention furthermore relates to the process for the preparation of the LC media according to the invention.

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It goes without saying to the person skilled in the art that the LC media according to the invention may also comprise compounds in which, for example, H, N, O, Cl, F have been replaced by the corresponding isotopes like deuterium etc.

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The following examples explain the present invention without restricting it. However, they show the person skilled in the art preferred mixture concepts with compounds preferably to be employed and the respective concentrations thereof and combinations thereof with one another. In addition, the examples illustrate which properties and property combinations are accessible.

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Preferred mixture components are shown in Table A below.

# Table A

In Table A, m and n are independently of each other an integer from 1 to 12, preferably 1, 2, 3, 4, 5 or 6, k is 0, 1, 2, 3, 4, 5 or 6, and (O) $C_mH_{2m+1}$  means  $C_mH_{2m+1}$  or  $OC_mH_{2m+1}$ .

$$C_{n}H_{2n+1} \longrightarrow F$$

AIK-n-F

10 
$$F$$
  $F$   $F$   $O$   $OC_mH_{2m+2}$   $O$   $OC_mH_{2m+2}$   $O$   $O$ 

$$C_{n}H_{2n+1}O - O - OC_{m}H_{2m+1}O - OC_{m}H$$

B-nO-O5i

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$$C_nH_{2n+1}$$
 $H$ 
 $O$ 
 $F$ 
 $O$ 
 $C_mH_{2m+1}$ 

BCH-nmF

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$$C_nH_{2n+1}$$
  $H$   $H$   $C_mH_{2m+1}$  BCN-nm

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$$C_nH_{2n+1}$$
  $H$   $O$   $OC_mH_{2m+1}$ 

CY-n-Om

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$$C_nH_{2n+1}$$
  $\longrightarrow$   $O$   $\longrightarrow$   $OC_mH_{2m+1}$ 

CY(F,CI)-n-Om

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$$C_{n}H_{2n+1} - \left(\begin{array}{c} CI & F \\ \hline \\ O \end{array}\right) - OC_{m}H_{2m+1}$$

CY(CI,F)-n-Om

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$$C_nH_{2n+1}$$
  $H$   $O$   $OC_mH_{2m+1}$ 

CCY-n-Om

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$$C_{n}H_{2n+1} - H - H - O - OC_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - H - O - OC_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - H - O - C_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - H - O - C_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - H - O - C_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - H - O - C_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - H - O - C_{m}H_{2m+1}$$

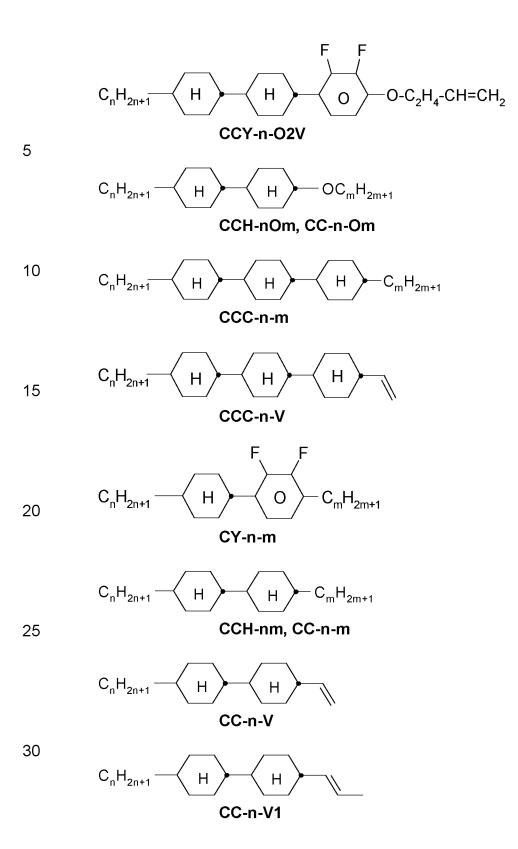
$$C_{n}H_{2n+1} - H - O - O - C_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - O - O - C_{m}H_{2m+1}$$

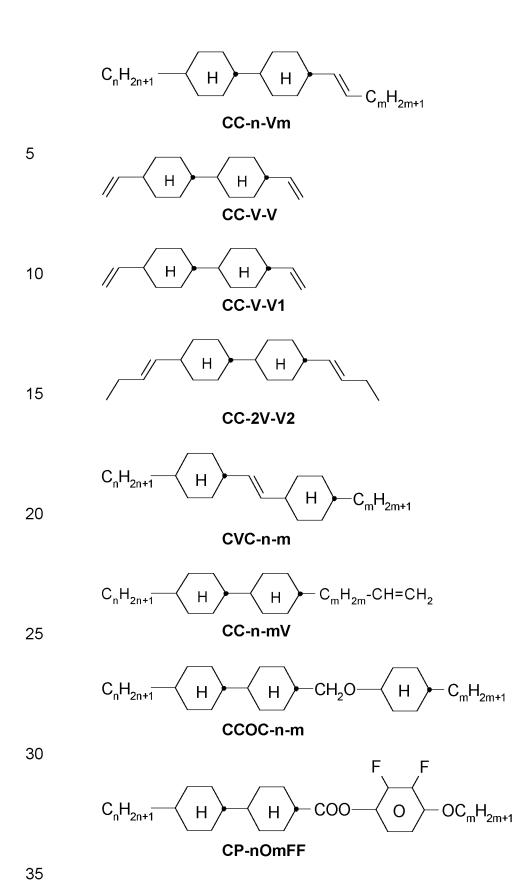
$$C_{n}H_{2n+1} - H - O - O - C_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - O - O - C_{m}H_{2m+1}$$

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$$C_nH_{2n+1}$$
  $H$   $COO$   $H$   $C_mH_{2m+1}$   $CH$ -nm

5 
$$F$$
  $F$   $C_nH_{2n+1}$   $H$   $C_2H_4$   $O$   $OC_mH_{2m+1}$   $CEY-n-Om$ 

10 
$$F$$
  $F$   $C_2H_4$   $O$   $C_nH_{2n+1}$ 

15 
$$CEY-V-n$$
 $F$ 
 $F$ 
 $O$ 
 $C_nH_{2n+1}$ 

CVY-V-n

$$\begin{array}{c|c}
 & F & F \\
\hline
 & O & OC_nH_{2n+1} \\
\hline
 & CY-V-On
\end{array}$$

$$C_{n}H_{2n+1} - \underbrace{H} O OCH_{2}CH = CH_{2}$$

$$CY-n-O1V$$

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$$C_{n}H_{2n+1} \longrightarrow H \longrightarrow O \longrightarrow CC = CH_{2}$$

$$CY-n-OC(CH_{3})=CH_{2}$$

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$$C_nH_{\overline{2n+1}}$$
 $H$ 
 $C_mH_{2m+1}$ 
 $CCN-nm$ 
 $F$ 
 $F$ 

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$$C_nH_{2n+1}$$
  $H$   $COO$   $O$   $H$   $C_mH_{2m+1}$   $CCPC-nm$ 

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$$C_{n}H_{2n+1} - H - O - (CH_{2})_{k}-OC_{m}H_{2m+1}$$

$$CCY-n-kOm$$

$$C_{n}H_{2n+1} - H - O - OC_{m}H_{2m+1}$$

$$CPY-n-Om$$

$$C_{n}H_{2n+1} - H - O - C_{m}H_{2m+1}$$

$$CPY-n-m$$

$$\begin{array}{c|c}
 & F & F \\
\hline
 & O & OC_mH_{2m+1} \\
\hline
 & CPY-V-Om
\end{array}$$

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$$C_nH_{2n+1}$$
  $H$   $CF_2O$   $O$   $C_mH_{2m+1}$   $CQY-n-(O)m$ 

$$C_nH_{2n+1}$$
  $H$   $OCF_2$   $O$   $C_mH_{2m+1}$ 

CQIY-n-(O)m

$$C_nH_{2n+1}$$
  $H$   $CF_2O$   $O$   $C_mH_{2m+1}$   $CCQY-n-(O)m$ 

$$C_nH_{2n+1}$$
  $H$   $OCF_2$   $O$   $O(O)C_mH_{2m+1}$   $CCQIY-n-(O)m$ 

$$C_nH_{2n+1}$$
  $H$   $O$   $CF_2O$   $O$   $O$   $CPQY-n-(O)m$ 

$$C_nH_{2n+1}$$
  $H$   $O$   $OCF_2$   $O$   $OCF_mH_{2m+1}$ 

CPQIY-n-(O)m

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CCY-V-Om

$$CCY-V-Om$$

$$COM$$

$$C$$

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$$C_{n}H_{2n+1} - H - O - O - C_{m}H_{2m+1}$$

$$CPGP-n-m$$

$$C_{n}H_{2n+1} - H - O - O - C_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - C_{n}H_{2n+1} - C_{n}H_{2$$

CENaph-n-Om

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 $C_nH_{2n+1} \qquad H \qquad O \qquad O \qquad C_mH_{2m+1}$ 

COChrom-n-m

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$$C_{n}H_{2n+1} \longrightarrow H \longrightarrow O \longrightarrow O \longrightarrow C_{m}H_{2m+1}$$

$$CCOChrom-n-m$$

$$F \longrightarrow F$$

$$C_{n}H_{2n+1} - H - O - O - OC_{m}H_{2m+1}$$

$$CONaph-n-Om$$

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$$C_{n}H_{2n+1} \longrightarrow H \longrightarrow O \longrightarrow OC_{m}H_{2m+1}$$

## CCNaph-n-Om

$$C_{n}H_{2n+1} - H - O - OC_{m}H_{2m+1}$$

CNaph-n-Om

$$C_nH_{2n+1} - H - OC_mH_{2m+1}$$

CETNaph-n-Om

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$$C_nH_{2n+1}$$
 $H$ 
 $O$ 
 $OC_mH_{2m+1}$ 
 $CTNaph-n-Om$ 

$$C_nH_{2n+1}$$
  $H$   $F$   $F$   $F$ 

10 **CK-n-F** 

$$C_nH_{2n+1}$$
  $H$   $O$   $OC_mH_{2m+1}$   $O$   $OC_mH_{2m+1}$ 

$$C_nH_{2n+1}$$
 $H$ 
 $CLY-n-m$ 
 $F$ 
 $F$ 
 $C_mH_{2m+1}$ 

$$C_nH_{2n+1} - C_mH_{2m+1}$$

25 LYLI-n-m

$$C_nH_{2n+1}$$
 $H$ 
 $O$ 
 $C_mH_{2m+1}$ 
 $CYLI-n-m$ 

$$C_{n}H_{2n+1} \longrightarrow O \longrightarrow (O)C_{m}H_{2m+1}$$

$$LY-n-(O)m$$

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$$C_{n}H_{2n+1} - H - C_{m}H_{2m+1}$$

$$COYOICC-n-m$$

$$COYOIC-n-V$$

$$COYOIC-n-V$$

$$COYOIC-n-V$$

$$COYOIC-n-V$$

$$COYOIC-n-V$$

$$COY-V-O2V$$

$$CCOY-V-O2V$$

$$C_{n}H_{2n+1} - H - CH_{2}O - OC_{m}H_{2m+1}$$

$$COY-n-Om$$

$$C_{n}H_{2n+1} - H - CH_{2}O - OC_{m}H_{2m+1}$$

$$COY-n-Om$$

$$C_{n}H_{2n+1} - H - COO - OC_{m}H_{2m+1}$$

D-nOmFF

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$$C_{n}H_{2n+1} - H - O - C_{m}H_{2m+1}$$

$$PCH-nm, CP-n-m$$

$$C_{n}H_{2n+1} - O - OC_{m}H_{2m+1}$$

$$PCH-nOm, CP-n-Om$$

$$C_{n}H_{2n+1} - O - O - C_{m}H_{2m+1}$$

$$PGP-n-m$$

$$C_{n}H_{2n+1} - O - C_{m}H_{2m+1}$$

$$PP-n-m$$

$$C_{n}H_{2n+1} - O - O - C_{m}H_{2m+1}$$

$$PP-n-m$$

$$C_{n}H_{2n+1} - O - O - C_{m}H_{2m+1}$$

$$PP-n-mV$$

$$C_{n}H_{2n+1} - O - O - C_{m}H_{2m+1}$$

$$PYP-n-mV$$

PYP-n-m

5

PY-n-m

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PY-V2-Om

$$C_nH_{2n+1} O O O C_mH_{2m+1}$$

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PY-V2-Om

 $C_nH_{2n+1}(O) O O O C_mH_{2m+1}$ 

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 $C_nH_{2n+1}(O) O O O C_mH_{2m+1}$ 

PY-nO-Om

 $C_nH_{2n+1}O O O O C_mH_{2m}$ 

Y-nO-OmV

 $C_nH_{2n+1}O O O O C_mH_{2m}$ 

Y-nO-OkVm

 $C_nH_{2n+1}O O O O C_mH_{2m}$ 

Y-nO-OkVm

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$$C_{n}H_{2n+1}O \longrightarrow O \longrightarrow OC_{m}H_{2m+1}$$

$$5 \qquad YG-nO-Om$$

$$C_{n}H_{2n+1} \longrightarrow O \longrightarrow OC_{m}H_{2m+1}$$

$$10 \qquad YGI-nO-Om$$

$$C_{n}H_{2n+1}O \longrightarrow O \longrightarrow OC_{m}H_{2m+1}$$

$$15 \qquad YGI-nO-Om$$

$$C_{n}H_{2n+1}O \longrightarrow O \longrightarrow OC_{m}H_{2m+1}$$

$$20 \qquad YY-n-Om$$

$$25 \qquad YY-nO-Om$$

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In a first preferred embodiment of the present invention, the LC media according to the invention, especially those with positive dielectric anisotropy, comprise one or more compounds selected from the group consisting of compounds from Table A1.

In a second preferred embodiment of the present invention, the LC media according to the invention, especially those with negative dielectric anisotropy, comprise one or more compounds selected from the group consisting of compounds from Table A2.

## Table B

Table B shows possible chiral dopants which can be added to the LC media according to the invention.

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$$C_2H_5$$
-CH-CH $_2$ O  $\bigcirc$ O  $\bigcirc$ CN  $CH_3$ 

C 15

**CM 21** 

**CM 44** 

 $C_2H_5$ -CH- $CH_2$ -O-O-O-CN

**CB 15** 

$$C_{6}H_{13}O \longrightarrow O \\ O \longrightarrow O \\ O - \overset{\star}{C}H_{13}$$

$$CH_{3}$$

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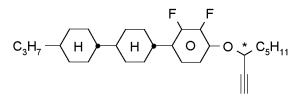
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**CM 45** 

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**CM 47** 

 $C_3H_7$  H O F  $CH_3$  O  $C_6H_13$ 



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The LC media preferably comprise 0 to 10% by weight, in particular 0.01 to 5% by weight, particularly preferably 0.1 to 3% by weight, of dopants. The LC media preferably comprise one or more dopants selected from the group consisting of compounds from Table B.

## Table C

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Table C shows possible stabilisers which can be added to the LC media according to the invention. Therein n denotes an integer from 1 to 12, preferably 1, 2, 3, 4, 5, 6, 7 or 8, and terminal methyl groups are not shown.

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$$HO \longrightarrow O \longrightarrow CH_2 \longrightarrow O \longrightarrow OH$$
  $HO \longrightarrow O \longrightarrow C \longrightarrow OH$   $HO \longrightarrow OH$   $HO \longrightarrow OH$   $HO \longrightarrow OH$   $HO \longrightarrow OH$ 

$$C_nH_{2n+1}$$
  $O$   $O$   $OH$ 

$$C_nH_{2n+1}$$
 O OH

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The LC media preferably comprise 0 to 10% by weight, in particular 1 ppm to 5% by weight, particularly preferably 1 ppm to 1% by weight, of stabilisers. The LC media preferably comprise one or more stabilisers selected from the group consisting of compounds from Table C.

## Table D

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Table D shows illustrative reactive mesogenic compounds which can be used in the LC media in accordance with the present invention.

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- 139 -

- 140 -

5 RM-58

10 RM-59

15 RM-60

20 RM-61

25 RM-62

RM-63

30 RM-64

- 145 -

- 146 -

RM-104

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15 F

RM-106

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25 o RM-107

RM-108 5 **RM**-109 10 15 **RM-110** 20 RM-111 25 RM-112 30

RM-113 5 RM-114 10 RM-115 15 RM-116 20 25 RM-117

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RM-152 5 RM-153 10 RM-154 15 RM-155 RM-156 20 RM-157 25 RM-158 30 **RM**-159 In a preferred embodiment, the mixtures according to the invention comprise one or more polymerizable compounds, preferably selected from the polymerizable compounds of the formulae RM-1 to RM-159. Of these, compounds RM-1, RM-4, RM-8, RM-17, RM-19, RM-35, RM-37, RM-39, RM-40, RM-41, RM-48, RM-52, RM-54, RM-57, RM-64, RM-74, RM-76, RM-88, RM-102, RM-103, RM-109, RM-116, RM-117, RM-120, RM-121, RM-122, R-139, RM-140, RM-142 and RM-146 to RM-154 are particularly preferred.

## Table E

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Table E shows self-alignment additives for vertical alignment which can be used in LC media for SA-VA and SA-FFS displays according to the present invention together with the polymerizable compounds of formula I:

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$$C_gH_{11}$$
 SA-12

 $C_gH_{11}$  SA-13

 $C_gH_{11}$  SA-14

 $C_gH_{11}$  SA-15

ОН ОН 5 SA-20 10 SA-21 15 20 ,OH OH SA-22 25

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In a preferred embodiment, the LC media, SA-VA and SA-FFS displays according to the present invention comprise one or more SA additives selected from formulae SA-1 to SA-48, preferably from formulae SA-14 to SA-48, very preferably from formulae SA-20 to SA-34 and SA-44, in combination with one or more RMs of formula I.

#### Examples

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The following examples explain the present invention without restricting it.

However, they show the person skilled in the art preferred mixture concepts

with compounds preferably to be employed and the respective concentrations thereof and combinations thereof with one another. In addition, the examples illustrate which properties and property combinations are accessible.

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In addition, the following abbreviations and symbols are used:

n<sub>e</sub> extraordinary refractive index at 20°C and 589 nm,

n<sub>o</sub> ordinary refractive index at 20°C and 589 nm,

10  $\Delta$ n optical anisotropy at 20°C and 589 nm,

 $\epsilon_{\perp}$  dielectric permittivity perpendicular to the director at 20°C and 1

kHz,

ε|| dielectric permittivity parallel to the director at 20°C and 1 kHz,

 $\Delta \varepsilon$  dielectric anisotropy at 20°C and 1 kHz,

15 cl.p., T(N,I) clearing point [°C],

γ<sub>1</sub> rotational viscosity at 20°C [mPa·s],

K<sub>1</sub> elastic constant, "splay" deformation at 20°C [pN],

K<sub>2</sub> elastic constant, "twist" deformation at 20°C [pN],

K<sub>3</sub> elastic constant, "bend" deformation at 20°C [pN].

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Unless explicitly noted otherwise, all concentrations in the present application are quoted in per cent by weight and relate to the corresponding mixture as a whole, comprising all solid or liquid-crystalline components, without solvents.

Unless explicitly noted otherwise, all temperature values indicated in the present application, such as, for example, for the melting point T(C,N), the transition from the smectic (S) to the nematic (N) phase T(S,N) and the clearing point T(N,I), are quoted in degrees Celsius (°C). M.p. denotes melting point, cl.p. = clearing point. Furthermore, C = crystalline state, N = nematic phase, S = smectic phase and I = isotropic phase. The data between these symbols represent the transition temperatures.

All physical properties are and have been determined in accordance with "Merck Liquid Crystals, Physical Properties of Liquid Crystals", Status Nov. 1997, Merck KGaA, Germany, and apply for a temperature of  $20^{\circ}$ C, and  $\Delta$ n is

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determined at 589 nm and  $\Delta\epsilon$  at 1 kHz, unless explicitly indicated otherwise in each case.

The term "threshold voltage" for the present invention relates to the capacitive threshold ( $V_0$ ), also known as the Freedericks threshold, unless explicitly indicated otherwise. In the examples, the optical threshold may also, as generally usual, be quoted for 10% relative contrast ( $V_{10}$ ).

Unless stated otherwise, the process of polymerizing the polymerizable compounds in the PSA displays as described above and below is carried out at a temperature where the LC medium exhibits a liquid crystal phase, preferably a nematic phase, and most preferably is carried out at room temperature.

Unless stated otherwise, methods of preparing test cells and measuring their electrooptical and other properties are carried out by the methods as described hereinafter or in analogy thereto.

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The display used for measurement of the capacitive threshold voltage consists of two plane-parallel glass outer plates at a separation of 25  $\mu$ m, each of which has on the inside an electrode layer and an unrubbed polyimide alignment layer on top, which effect a homeotropic edge alignment of the liquid-crystal molecules.

The PSVA display or PSVA test cell used for measurement of the tilt angles consists of two plane-parallel glass outer plates at a separation of 4  $\mu$ m unless stated otherwise, each of which has on the inside an electrode layer and a polyimide alignment layer on top, where the two polyimide layers are rubbed antiparallel to one another and effect a homeotropic edge alignment of the liquid-crystal molecules. The SAVA display or test cell has the same structure but wherein one or both polyimide layers are omitted.

The polymerizable compounds are polymerized in the display or test cell by irradiation with UV light of defined intensity for a prespecified time, with a voltage simultaneously being applied to the display (usually 10 V to 30 V alternating current, 1 kHz). In the examples, unless indicated otherwise, a metal halide lamp and an intensity of 100 mW/cm² is used for polymerization.

The intensity is measured using a standard meter (Hoenle UV-meter high end with UV sensor).

The tilt angle is determined using the Mueller Matrix Polarimeter "AxoScan" from Axometrics. A low value (i.e. a large deviation from the 90° angle) corresponds to a large tilt here.

Unless stated otherwise, the term "tilt angle" means the angle between the LC director and the substrate, and "LC director" means in a layer of LC molecules with uniform orientation the preferred orientation direction of the optical main axis of the LC molecules, which corresponds, in case of calamitic, uniaxially positive birefringent LC molecules, to their molecular long axis.

#### Example 1

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Compound 1 is prepared as follows

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a) Synthesis of bromide A

50.00 g (277.40 mmol) 9,10-Dihydrophenanthrene is dissolved in 750 mL

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Dichloromethane and 510.00 mg (3.14 mmol) Iron powder is added and the mixture is cooled to 5°C. 30.00 mL (585.70 mmol)  $Br_2$  dissolved in 450 mL dichloromethane is being added dropwise and the reaction mixture is stirred over night at room temperature. The surplus  $Br_2$  is quenched by adding dropwise NaHSO<sub>3</sub> solution. Additional water is being added and the layers are separated. The organic layer is washed with  $Na_2S_2O_3$  solution, dried over

Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under vacuum. The product is crystallized with acetone.

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, J = 8.3 Hz, 2H), 7.44 (dd, J = 8.4, 1.9 Hz, 2H), 7.41 (d, J = 1.9 Hz, 2H), 2.86 (s, 4H).

#### b) Synthesis of boronic acid B

5.50 g (19.95 mmol) bromide **A** and 5.20 mL (22.67 mmol) triisopropyl borate are dissolved in 80 mL THF, cooled with dry ice to -50°C and n-buthyllithium (1.6 M in hexane) is added slowly so that the temperature does not exceed minus 45°C. The reaction mixture is stirred for 60 min at minus 50°C. The reaction mixture is quenched with 50 mL 2N HCl and is carefully poured on 50 mL 2N HCl and methyl tert-butyl ether (MTBE). The layers are separated, the water layer is extracted with MTBE and the combined organic layers are washed with water, brine and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under vacuum to yield an colorless reaction product which is directly used in the next synthesis transformation.

#### c) Synthesis of alcohol C

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6.30 g (11.0 mmol, 51%) is dissolved in 50.0 mL THF and a mixture of 2.20 mL water and 1.70 mL acetic acid (100%) is added. 2.50 mL  $H_2O_2$  (29.07 mmol, 35% solution water) is added dropwise and the exothermic reaction is cooled with an ice water cooling bath. The mixture is stirred for 17h at room temperature. Water is added and the mixture is extracted with MTBE. The

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combined organic layers are washed several times with ammonium iron (II) sulfate to remove the remaining H<sub>2</sub>O<sub>2</sub>. The organic layer is then washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under vacuum. The crude product is filtered with dichloromethane over silica gel, combined and evaporated under vacuum to give the product a yellow, crystalline solid.

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.35 – 7.24 (m, 2H), 6.70 (dd, J = 8.4, 2.7 Hz, 1H), 6.64 (d, J = 2.7 Hz, 1H), 4.68 (s, 1H), 2.89 – 2.54 (m, 4H).

d) Synthesis of boronic ester **D** 

2.40 g (8.42 mmol) alcohol **C**, 2.40 g (9.45 mmol) bis(pinacolato)boron and 3.30 g (23.44 mmol) KOAc are dissolved in 25 mL 1,4-dioxane. 0.20 g (0.27 mmol) Pd(dppf)Cl<sub>2</sub> is added and the reaction is stirred under reflux for 5h. It is cooled to room temperature and the reaction mixture is poured on 2N HCl and acetic acid ethylester (EE). The organic layer is washed with water and brine and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under vacuum. The product is purified by column chromatography with dichloromethane and the combined product is evaporated under vacuum to yield a colorless oil.

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.75 (dd, J = 7.7, 1.2 Hz, 1H), 7.71 – 7.65 (m, 3H), 6.80 (dd, J = 8.4, 2.7 Hz, 1H), 6.74 (d, J = 2.7 Hz, 1H), 4.82 (s, 1H), 2.89 (dd, J = 8.4, 4.8 Hz, 2H), 2.83 (dd, J = 9.5, 5.6 Hz, 2H), 1.39 (s, 12H).

e) Synthesis of bis-alcohol E

1.60 g (7.64 mmol) 4-bromo-3-methoxyphenol are dissolved in 20.0 mL THF and 1.60 g (11.57 mmol)  $K_2CO_3$  are being added with 10 mL water. The mixture is degassed with Argon for 30 min and the mixture is heated to 65°C. 50.00 mg (0.14 mmol) CataCxium A and 65.00 mg (0.07 mmol)  $Pd_2(dba)_3$  is added. 2.30 g (6.90 mmol) of boronic ester E (dissolved in 20 mL THF) is added dropwise and the mixture is stirred for 2.5 h under reflux. The mixture is cooled to room temperature and the organic layer is separated. The water layer is extracted with EE and the combined organic layer is washed with brine, dried over  $Na_2SO_4$ , filtered and evaporated under vacuum. The product is filtered over silica gel with dichloromethane and MTBE (1:1) and crystallized out of MTBE.

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 2H), 7.63 (dd, J = 10.2, 8.2 Hz, 2H), 7.30 (dd, J = 8.1, 2.0 Hz, 1H), 7.25 (d, J = 1.8 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 6.71 (dd, J = 8.3, 2.6 Hz, 1H), 6.67 (d, J = 2.6 Hz, 1H), 6.51 (d, J = 2.3 Hz, 1H), 6.44 (dd, J = 8.2, 2.2 Hz, 1H), 3.72 (s, 3H), 2.84 – 2.66 (m, 4H).

 $MS [APCI] 319.13 = M+H^+$ 

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## f) Synthesis of compound 1

3.40 g (10.00 mmol) bisalcohol **E,** 2.60 mL (30.65 mmol) methacrylic acid (stabilized, Merck 800578), 0.25g (2.05 mmol) 4-(dimethylamino)-pyridine are dissolved in 100 mL dichloromethane and cooled to 2°C. 5.20 mL (30.15 mmol) 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide is added dropwise and the reaction mixture is stirred over night at room temperature. The reaction

mixture is filtered over 150g silica gel and 100g alox (basic) with dichloromethane. The reaction product is evaporated under vacuum and crystallized with MTBE to yield the product as a colorless solid.

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.44 (dd, J = 8.0, 1.9 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.17 – 7.09 (m, 2H), 6.99 (d, J = 2.2 Hz, 1H), 6.86 (dd, J = 8.2, 2.2 Hz, 1H), 6.31 (dt, J = 7.3, 1.3 Hz, 2H), 5.93 (dq, J = 5.4, 1.6 Hz, 2H), 3.79 (s, 3H), 2.88 (s, 4H), 2.03 (dt, J = 5.1, 1.3 Hz, 6H).

 $MS [APCI] 455.18 = M+H^{+}$ 

The absorption wavelength  $\lambda$  of compound **1** at an extinction coefficient of E = 0.5 is measured as 357nm for a solution in DCM at a concentration of 3g/L.

Examples 2-5

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Compounds 2 to 5 are prepared in analogy to Example 1.

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## 15 Use Example A - Comparison of Physical Properties

The absorption wavelength  $\lambda$  at an extinction coefficient of E = 0.5 is determined for compound RM-1 of prior art by the method as described in Example 1. This wavelength is useful to characterize the wavelength dependence of the UV photopolymerization of the compound.

The UV absorption wavelength of compounds 1 and 2 of Example 1 and 2 are compared with that of compound RM-1 of prior art. The results are shown in Table 1.

## Table 1 –UV Absorption

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		RM-1	1	2
35	UV absorption wavelength $\lambda$ (nm) at E=0.5	320	357	361

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From Table 1 it can be seen that compounds 1 and 2 according to the invention have a long absorption wavelength, which is higher than that of compound RM-1. Compounds 1 and 2 are thus especially suitable for UV photopolymerization at longer wavelengths or faster polymerization at shorter wavelengths.

#### Polymerizable Mixtures

The nematic LC host mixture N1 is formulated as follows

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	B(S)-20-04	4.50 %	cl.p.	76°C
	B(S)-20-05	5.00 %	$\Delta n$	0.1120
	BCH-32	6.00 %	$\Delta arepsilon$	-3.0
	CC-3-V	47.50 %	$\epsilon_{\parallel}$	3.5
15	CLY-3-O2	6.00 %	$\gamma_1$	74 mPa⋅s
	CPY-2-O2	10.50 %	$K_1$	14.2
	CPY-3-O2	10.50 %	K <sub>3</sub>	14.5
	PY-1-02	10.00 %	$K_3/K_1$	1.06
			$V_0$	2.31 <b>V</b>

Polymerizable mixture P1.1 is prepared by adding the polymerizable compound 1 of Example 1 to the nematic LC host mixture N1 at a concentration of 0.3%.

- Polymerizable mixture P1.2 is prepared by adding the polymerizable compound 1 of Example 1 to the nematic LC host mixture N1 at a concentration of 0.45%.
- Polymerizable mixture P1.3 is prepared by adding the polymerizable compound 2 of Example 2 to the nematic LC host mixture N1 at a concentration of 0.3%.

Polymerizable mixture P1.4 is prepared by adding the polymerizable compound 2 of Example 2 to the nematic LC host mixture N1 at a concentration of 0.45%.

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#### Low Temperature Stability (LTS)

The LTS of compounds 1 and 2 is measured in the host mixture N1. The results are shown in Table 2.

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## Table 2 - LTS

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Mixture	LTS	
Mixture	(-20°C)	
P1.1	792h	
P1.2	624h	
P1.3	576h	
P1.4	480h	

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It can be seen that compounds 1 and 2 have a good LTS in the nematic host N1 even at a higher concentration of 0.45% (P1.2 and P1.4).

## <u>Use Example B – Polymerizable Mixtures</u>

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For comparison purposes the polymerizable reference mixture C1 is prepared by adding compound RM-1 of prior art to the nematic LC host mixture N1 at a concentration of 0.3%.

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Based on the UV-Vis absorption data shown in Table 1 above, it is obvious that compound RM-1 will not react with UV-LED emission centered around 365 nm because of the lack of overlap of absorption with the UV-LED emission. Therefore, in the following the polymerization of compound RM-1 is carried out with a C-type fluorescent lamp having an emission peak at 313 nm, while compounds 1 and 2 are polymerized with an UV-LED lamp showing emission centered around 365 nm.

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For polymerization of poymerizable compounds 1 and 2 test cells containing the polymerizable mixture are exposed to UV light in a two step process. In UV1 step a voltage is applied (20  $V_{pp}$  square wave, 200 Hz). In UV2 step no voltage is applied. The other conditions are as follows:

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UV1 (LED lamp): 20 mW/cm<sup>2</sup> at room temperature, 210s for 0.45%; 325s for 0.3%

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UV2 (LED lamp): 10 mW/cm<sup>2</sup> at RT, 180 min

For polymerization of the polymerizable compound RM-1 test cells containing the polymerizable mixture are irradiated using conventional lamps to polymerize the compound in two steps as described above. The conditions are as follows.

UV1 (C-type fluorescent lamp): 4.5 mW/cm² at room temperature, 150s UV2 (C-type fluorescent lamp): 0.5 mW/cm² at room temperature, 120 min

# Tilt Stability

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Tilt stability, i.e. the change of the tilt angle after repeated electric stress, is a criterion for evaluating the risk of image sticking. A low value for the change of the tilt angle indicates a high tilt stability and a low potential risk of image sticking.

For determining the tilt stabillity the test cells after polymerization as described above are electrically stressed with a square wave of 60V<sub>PP</sub> at 60 Hz for 72 h. After a relaxation time of 5-10 min the tilt angles are measured using the Otsuka T\_RETS-10 system.

The change of the tilt angle  $\Delta tilt$  is determined according to equation (1)

$$tilt_{after stress} - tilt_{after tilt generation} = \Delta tilt$$
 (1)

and is shown in Table 3 below.

The lower the value of \( \Delta tilt \), the higher is the tilt stability.

## 30 Table 3 – Tilt Stability

Mixture	∆tilt / °
C1*	0.5
P1.1**	0.7
P1.2**	0.5
P1.4**	0.5

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- \* UV C-type fluorescent lamp
- \*\* 365 nm UV-LED lamp

From Table 3 it can be seen that polymerizable mixtures P1.1, P1.2 and P1.4 according to the invention show good tilt stability.

## Voltage Holding Ratio (VHR)

The VHR of the polymerisable LC media is measured at 60°C with application of a voltage of 1 V / 0.6 Hz initial and after UV exposure. Light stress usually causes the decrease of VHR in LC mixtures, therefore the smaller the absolute decrease of VHR value after stress, the better performance for display applications.

The results are shown in Table 4.

Table 4 - VHR

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Mixture	VHR (%)	VHR (%)
Mixture	Initial	after 2h UV
C1*	99.6	76.2
P1.1**	99.7	88.1
P1.2**	99.7	97.1
P1.3**	99.7	88.4
P1.4**	99.7	88.9

\* UV C-type fluorescent lamp

\*\* 365 nm UV-LED lamp

From Table 4 it can be seen that the VHR values of the polymerizable mixtures P1.1 to P1.4 according to the invention are significantly higher than that of polymerizable mixture C1 especially when using a higher concentration of compound 1 or 2.

Overall the results demonstrate that the polymerizable compounds of formula I are suitable for use in PSA displays prepared by a polymerization process using long UV wavelengths >350nm, and especially using UV-LED lamps.

## **Claims**

## 1. A compound of formula I

 $R^{a}-(A^{a}-Z^{a})_{a} - (Z^{b}-A^{b})_{b}-R^{b}$ 

wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

Ra, Rb P-Sp- or R, wherein at least one of Ra and Rb denotes P-Sp-,

A<sup>a</sup>, A<sup>b</sup> phenylene-1,4,-diyl or naphthalene,2-6-diyl which is optionally substituted by one or more groups L,

 $Z^a$ ,  $Z^b$  -CH=CH-, -CF=CF-, -C $\equiv$ C- or a single bond,

P a polymerizable group,

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Sp a spacer group that is optionally substituted by one or more groups P, or a single bond,

R straight chain, branched or cyclic alkyl having 1 to 25 C atoms, wherein one or more non-adjacent CH<sub>2</sub>-groups are optionally replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-,

that O- and/or S-atoms are not directly connected with each other, and wherein one or more H atoms are each optionally replaced by F or Cl,

L F, Cl, Br, -CN or straight chain, branched or cyclic alkyl having 1 to 25 C atoms, wherein one or more non-adjacent CH<sub>2</sub>-groups

are optionally replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-, -N( $R^0$ )-, -Si( $R^0R^{00}$ )-, -CH=CH- or -C $\equiv$ C- in such a manner that O- and/or S-atoms are not directly connected with each other, and wherein one or more H atoms are each optionally replaced by F or CI,

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R<sup>0</sup>, R<sup>00</sup> H or alkyl with 1 to 12 C atoms,

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a, b 0, 1 or 2, preferably 0 or 1,

r1 0, 1, 2, 3 or 4, preferably 0, 1 or 2.

2. The compound according to Claim 1, which is selected from formula I1

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wherein P, Sp, L and r1 have independently of each other one of the meanings given in claim 1.

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3. The compound according to Claim 1 or 2, which is selected from the following subformulae:

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- 4. An LC medium comprising one or more compounds according to one or more of Claims 1 to 3.
  - 5. The LC medium according to Claim 4, characterized in that it additionally comprises one or more compounds of formula II

$$L^{1}$$
 $L^{2}$ 
 $R^{1}$ 
 $(Z^{2}$ 
 $A^{2})_{a2}$ 
 $R^{2}$ 

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wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

R¹ and R² straight chain, branched or cyclic alkyl having 1 to 25 C atoms, wherein one or more non-adjacent CH₂-groups are optionally replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-

manner that O- and/or S-atoms are not directly connected with each other, and wherein one or more H atoms are each optionally replaced by F or Cl, preferably alkyl or alkoxy having 1 to 6 C atoms,

R<sup>0</sup>, R<sup>00</sup> H or alkyl with 1 to 12 C atoms, preferably H,

A<sup>1</sup> and A<sup>2</sup> a group selected from the following formulae

wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

10  $Z^1 \text{ and } Z^2 \text{ -CH}_2\text{CH}_2\text{--, -CH}=\text{CH}_-, \text{ -CF}_2\text{O}_-, \text{ -OCF}_2\text{--, -CH}_2\text{O}_-, \text{ -OCH}_2\text{--, -CO}_2\text{---, -CF}=\text{CF}_-, \text{ -CH}=\text{CH}_2\text{O}_- \text{ or a single bond, preferably a single bond,}$ 

L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup> and L<sup>4</sup> F, Cl, OCF<sub>3</sub>, CF<sub>3</sub>, CH<sub>3</sub>, CH<sub>2</sub>F or CHF<sub>2</sub>, preferably F or Cl, very preferably F,

Y H, F, Cl, CF<sub>3</sub>, CHF<sub>2</sub> or CH<sub>3</sub>, preferably H or CH<sub>3</sub>, very preferably H,

L<sup>C</sup> CH<sub>3</sub> or OCH<sub>3</sub>, preferably CH<sub>3</sub>,

a1 1 or 2,

a2 0 or 1.

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 The LC medium according to one or more of Claims 4 or 5, characterized in that it contains one or more compounds of formula II selected from the group consisting of compounds of the formulae IIA, IIB, IIC and IID

$$R^{2A}$$
  $IIA$   $IIA$ 

$$R^{2A} - Z^2 - Z^{2B} - Z^{2B} - R^{2B}$$
IIB

$$R^{2A}$$
  $R^{2B}$  IIC

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$$R^{2A}$$
  $Z^{2}$   $Z^{2D}$   $R^{2B}$  IID

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in which

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R<sup>2A</sup> and R<sup>2B</sup> each, independently of one another, denote H, an alkyl or alkenyl radical having up to 15 C atoms which is unsubstituted, monosubstituted by CN or CF<sub>3</sub> or at least monosubstituted by halogen, where, in addition, one or more CH<sub>2</sub> groups in these

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 $-C \equiv C$ -,  $-CF_2O$ -,  $-OCF_2$ -, -OC-O- or -O-CO- in such a way that O atoms are not linked directly to one another,

 $\mathsf{L}^1$  to  $\mathsf{L}^4$  each, independently of one another, denote F, Cl, CF3 or CHF2,

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Y denotes H, F, Cl, CF<sub>3</sub>, CHF<sub>2</sub> or CH<sub>3</sub>, preferably H or CH<sub>3</sub>, particularly preferably H,

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Z<sup>2</sup>, Z<sup>2B</sup> and Z<sup>2D</sup> each, independently of one another, denote a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH=CH-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -COO-, -OCO-, -C<sub>2</sub>F<sub>4</sub>-, -CF=CF-, -CH=CHCH<sub>2</sub>O-,

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- p denotes 0, 1 or 2, and
- q on each occurrence, identically or differently, denotes 0 or 1.

7. The LC medium according to one or more of Claims 4 to 6, characterized in that it additionally comprises one or more compounds of formula III

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$$R^{11}-(A^3-Z^1)_n$$
  $R^{12}$ 

in which

R<sup>11</sup> and R<sup>12</sup> each, independently of one another, denote H, an alkyl or alkoxy radical having 1 to 15 C atoms, where one or more CH<sub>2</sub> groups in these radicals may each be replaced,

independently of one another, by , , , , ,

O-, -CO-O- or -O-CO- in such a way that O atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by halogen,

A<sup>3</sup> on each occurrence, independently of one another, denotes

- a) 1,4-cyclohexenylene or 1,4-cyclohexylene radical, in which one or two non-adjacent CH<sub>2</sub> groups may be replaced by -O- or -S-,
- b) a 1,4-phenylene radical, in which one or two CH groups may be replaced by N, or
- c) a radical selected from the group consisting of spiro[3.3]heptane-2,6-diyl, 1,4-bicyclo[2.2.2]octylene,

naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl, 1,2,3,4-tetrahydronaphthalene-2,6-diyl, phenanthrene-2,7diyl and fluorene-2,7-diyl,

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wherein the radicals a), b) and c) may be mono- or polysubstituted by halogen atoms,

n

 $Z^1$ 

denotes 0, 1 or 2, preferably 0 or 1,

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on each occurrence independently of one another denotes -CO-O-, -O-CO-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -(CH<sub>2</sub>)<sub>4</sub>-, -CH=CH-CH<sub>2</sub>O-, -C<sub>2</sub>F<sub>4</sub>-, -CH<sub>2</sub>CF<sub>2</sub>-, - $CF_2CH_2$  -, -CF=CF-, -CH=CF-, -CF=CH-,  $-C\square C$ - or a single bond.

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 $L^{11}$  and  $L^{12}$ 

8.

each, independently of one another, denote F, Cl, CF<sub>3</sub> or CHF<sub>2</sub>, preferably H or F, most preferably F, and

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W denotes O or S.

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The LC medium according to to one or more of Claims 4 to 7, characterized in that it additionally comprises one or more compounds of formula IV

$$R^{41}$$
  $R^{42}$   $IV$ 

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in which

 $R^{41}$ denotes an unsubstituted alkyl radical having 1 to 7 C atoms or an unsubstituted alkenyl radical having 2 to 7 C atoms, preferably an *n*-alkyl radical, particularly preferably having 2, 3, 4 or 5 C atoms, and

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R<sup>42</sup> denotes an unsubstituted alkyl radical having 1 to 7 C atoms or an unsubstituted alkoxy radical having 1 to 6 C atoms, both preferably having 2 to 5 C atoms, an unsubstituted alkenyl radical having 2 to 7 C atoms, preferably having 2, 3 or 4 C atoms, more preferably a vinyl radical or a 1-propenyl radical and in particular a vinyl radical.

9. The LC medium according to one or more of Claims 4 to 8, characterized in that it additionally comprises one or more compounds of formula V

$$R^{51}$$
  $Z^{51}$   $A^{51}$   $Z^{52}$   $A^{52}$   $R^{52}$   $V$ 

in which 15

> R<sup>51</sup> and R<sup>52</sup> independently of one another, have one of the meanings given for R<sup>41</sup> and R<sup>42</sup> and preferably denote alkyl having 1 to 7 C atoms, preferably n-alkyl, particularly preferably n-alkyl having 1 to 5 C atoms, alkoxy having 1 to 7 C atoms, preferably n-alkoxy, particularly preferably n-alkoxy having 2 to 5 C atoms, alkoxyalkyl, alkenyl or alkenyloxy having 2 to 7 C atoms, preferably having 2 to 4 C atoms, preferably alkenyloxy,

Z<sup>51</sup>, Z<sup>52</sup> each, independently of one another, denote -CH<sub>2</sub>-CH<sub>2</sub>-, -CH<sub>2</sub>-O-,-CH=CH-, -C≡C-, -COO- or a single bond, preferably -CH<sub>2</sub>-CH<sub>2</sub>-, -CH<sub>2</sub>-O- or a single bond and particularly preferably a single bond, and

n is 1 or 2.

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10. The LC medium according to one or more of Claims 4 to 9, characterized in that it additionally comprises one or more additives selected from the group consisting of stabilizers, chiral dopants, polymerization initiators and self alignment additives.

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11. A process of preparing an LC medium according to one or more of Claims 1 to 10, comprising the steps of mixing one or more one or more polymerizable compounds as defined in one or more of Claims 1 to 3 with one or more compounds of formula II, III, IV and/or V as defined in one or more of Claims 4 to 9, and optionally with further liquid-crystalline compounds and/or additives, and optionally polymerizing the polymerizable compounds.

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- 12. An LC display comprising a compound as defined in one or more of Claims 1 to 3 or comprising an LC medium as defined in one or more of Claims 4 to 10.
- 13. The LC display according to Claim 12, which is a PSA or SA display.

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14. The LC display according to Claim 13, which is a PS-VA, PS-IPS, PS-FFS or SA-VA display.

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15. The LC display according to Claim 13 or 14, characterized in that it comprises two substrates, at least one of which is transparent to light, an electrode provided on each substrate or two electrodes provided on only one of the substrates, and located between the substrates a layer of an

LC medium according to one or more of Claims 4 to 10, wherein the polymerizable compounds are polymerized between the substrates of the display by UV photopolymerization.

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16. A process for the production of an LC display according to Claim 15, comprising the steps of providing an LC medium according to one or more of Claims 4 to 10 between the substrates of the display, and polymerizing the polymerizable compounds by irradiation with UV light, preferably while a voltage is applied to the electrodes of the display.

17. The process according to Claim 16, characterized in that the UV light has a wavelength >360 nm.

18. The process according to Claim 17, characterized in that the UV light has a wavelength in the range from 360 to 380 nm.

19. The process according to one or more of Claims 16 to 18, characterized in that irradiation with UV light is carried out using an UV-LED lamp.

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## **INTERNATIONAL SEARCH REPORT**

International application No
PCT/EP2021/080459

A. CLASSIFICATION OF SUBJECT MATTER									
1	C09K19/32 C09K19/34 C09K19	9/30 C09K19/12 C	09K19/04						
ADD.									
According to International Patent Classification (IPC) or to both national classification and IPC									
B. FIELDS SEARCHED									
Minimum documentation searched (classification system followed by classification symbols)  C09K									
COOK									
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched									
Electronic c	data base consulted during the international search (name of data	base and, where practicable, search terms t	ised)						
EPO-In	nternal, WPI Data, CHEM ABS Data								
C. DOCUMENTS CONSIDERED TO BE RELEVANT									
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LLI Furt	her documents are listed in the continuation of Box C.	See patent family annex.							
* Special of	categories of cited documents :	"T" later document published after the inte	ernational filing date or priority						
A" docum	ent defining the general state of the art which is not considered	date and not in conflict with the appli the principle or theory underlying the	cation but cited to understand						
to be	of particular relevance	the principle of theory underlying the	rinvention						
E" earlier:	application or patent but published on or after the international date	"X" document of particular relevance;; the considered novel or cannot be consi							
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	to establish the publication date of another citation or other all reason (as specified)	"Y" document of particular relevance;; the considered to involve an inventive st							
	ent referring to an oral disclosure, use, exhibition or other	combined with one or more other su- being obvious to a person skilled in t	ch documents, such combination						
mean: "P" docume	ne art								
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Date of the	Date of the actual completion of the international search  Date of mailing of the international search report								
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NL - 2280 HV Rijswijk									
	Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schoenhentz, Jér	ôme						

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