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☐ Drawing(s) : paged to paged	
☒ Abstract : paged to paged	
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Ref. 6220/125

5 The present invention is concerned with photo cross-linkable, optically active compounds, liquid crystalline mixtures which contain such compounds as well as their use in the cross-linked state as optical components.

10 Photo cross-linkable liquid crystals, which are provided with a suitable amount of a photoinitiator, can be oriented on a substrate or in a cell by suitable orienting layers or in a field and then in this state can be cross-linked by irradiation with light of a suitable wavelength. The structure thereby produced is
 15 preserved even at high temperatures. Thus, optical components such as, for example, wave guides, optical grids and filters, piezoelectric cells and cells having non-linear optical (NLO) properties, electro-optical devices, etc. can be produced. Such optical components can be used, for example, in cells for
 20 frequency doubling (SHG) or in colour filters.

Further properties such as, for example, the birefringence, the refractive index, the transparency, etc. must fulfil different requirements depending on the field of use. For example,
 25 materials for colour filters, polarizers, $\lambda/2$ plates, etc. should produce a small pitch for circularly polarized light.

The photo cross-linkable liquid crystals must have a good chemical and thermal stability, good solubility in usual solvents
 30 and a good stability towards electric fields and electromagnetic radiation. They should have a suitable mesophase in a temperature range from about 25°C to about +100°C, especially from about 25°C to about +80°C.

35 Chiral nematic (cholesteric) liquid crystals in the homogeneously orientated state (Grandjean texture) reflect light essentially only in a wavelength range which is dependent on the wavelength of the helical pitch. The spectral width of this

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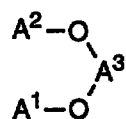
reflected light can be varied by suitable choice of the liquid crystal. The reflected light is completely circularly polarized. The direction of rotation of the reflected light depends on the direction of rotation of the cholesteric helical structure. The oppositely circularly polarized light is transmitted unimpaired. These properties can be used for the production of optical filters, polarizers, analyzers, etc. When such cholesteric mixtures contain photochemically oligomerisable or polymerisable components, then these components can be cross-linked by irradiation with light. The liquid crystalline structure of these mixtures is thereby stabilized or even frozen. Thus, colour filters, $\lambda/2$ plates, optical retarders, polarizers, etc. can be produced in the solid state.

Since liquid crystals are usually used as mixtures of several components, it is important that the components have a good miscibility with one another. Mixtures consisting of photo cross-linkable liquid crystals and non-photo cross-linkable components, which lead to optical activity in mixtures, allow the non-cross linked components to relax and thereby decrease the stability of the network. Conventional optically active photochemically oligomerizable or polymerisable additives have the centre of chirality in the spacers between the photo cross-linkable group and the core of the molecule. This requires an expensive and complicated synthesis. The twisting capacity of these compounds is relatively small.

There is accordingly the need to produce, especially for use in optical filters, photochemically oligomerisable or polymerisable optically active compounds which have a large twisting capacity. Thus, they can be admixed in liquid crystalline mixtures in small concentrations in order to produce the desired pitch without influencing the clearing point or other physical properties of the mixture too severely. Moreover, they should be readily accessible from starting materials which are known or which are commercially available. Furthermore, mixtures which contain such optically active photo cross-linkable compounds should be orientable and structurable as domain-free as possible

and should also have an excellent thermal stability and long-term stability in the cross-linked state.

The present invention now provides compounds which are
 5 outstandingly suitable as single components or as components of
 such liquid crystal mixtures. The compounds of the present
 invention have general formula I



I

10

wherein

A¹ and A² each signify a cross-linkable mesogenic
 residue; and

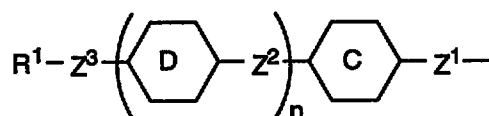
A³ signifies (R,R)- or (S,S)-trans-1,2-
 15 cyclohexyl-diyl.

15

Since the compounds of formula I in accordance with the
 invention or mixtures containing such compounds have a meso-
 phase, they can, prior to the cross-linking, be oriented on an
 20 orienting layer by the application of an electric or magnetic field.
 A uniform layer is produced in this manner.

Preferably, the mesogenic residues A¹ and A² each signify a
 residue of general formula II

25

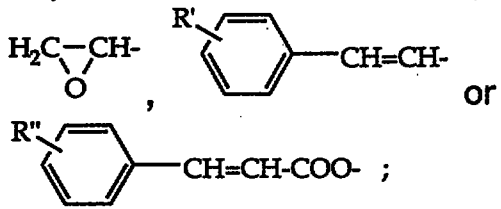


II

wherein

30 rings C and D each independently signify pyridine-2,5-
 diyl, pyrimidine-2,5-diyl, trans-1,4-
 cyclohexylene, trans-1,3-dioxane-2,5-diyl
 or 1,4-phenylene optionally substituted
 with halogen, methyl and/or cyano;
 Z¹ signifies -(CH₂)_m-, -CO-, -(CH₂)_mCO- or
 35 -(CH₂)_mOOC-;

35

	Z ²	signifies a single bond, -CH ₂ CH ₂ -, -CH ₂ O-, -OCH ₂ -, -COO-, -OOC-, -(CH ₂) ₄ -, -O(CH ₂) ₃ - or -(CH ₂) ₃ O-;
5	Z ³	-(CY ₂) _m -, -O(CY ₂) _m -, -(CY ₂) _m O-, -(CY ₂) _m COO-, -(CY ₂) _m OOC-, -(Si[(CH ₃) ₂]O) _m -, -OCH ₂ (Si[(CH ₃) ₂]O) _m -, Si[(CH ₃) ₂]CH ₂ O- or -NHCH ₂ (Si[(CH ₃) ₂]O) _m -, Si[(CH ₃) ₂]CH ₂ NH-;
	Y	signifies hydrogen or fluorine;
10	n	signifies 0, 1 or 2;
	m	signifies a whole number of 1 to 16; and
	R ¹	signifies a cross-linkable group of the structure CH ₂ =CH-, CH ₂ =CH-COO-, CH ₂ =C(CH ₃)-COO-, CH ₂ =C(Cl)-COO-, CH ₂ =C(Ph)-COO-, CH ₂ =CH-COO-Ph-, CH ₂ =CH-CO-NH-, CH ₂ =C(CH ₃)-CONH-, CH ₂ =C(Cl)-CONH-, CH ₂ =C(Ph)-CONH-, CH ₂ =C(COOR')-CH ₂ -COO-, CH ₂ =CH-O-, CH ₂ =CH-OOC-, Ph-CH=CH-, CH ₃ -C(=NR')-,
15		cis,trans HOO-CR'=CR'-COO-,
20		
	Ph	signifies phenyl;
25	R'	signifies lower alkyl; and
	R''	signifies methyl, methoxy, cyano or halogen;

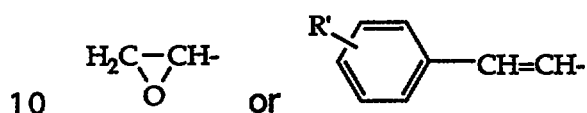
with the proviso that R¹-Z³ contains no -O-O- or -N-O- groups.

- 30 Compounds of formula I in which the two mesogenic residues A¹ and A² have the same significance are preferred.

- 35 Residues A¹ and A² of formula II in which rings C and D each independently signify unsubstituted or fluoro-substituted 1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl or trans-1,4-cyclohexylene, Z¹ signifies -CH₂-, -CO- or -OOC-, Z² signifies a

single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{OCH}_2-$, $-\text{COO}-$ or $-\text{OOC}-$, Z^3 signifies $-(\text{CH}_2)_m-$, $-(\text{CH}_2)_m\text{O}-$, $-(\text{CH}_2)_m\text{COO}-$ or $-(\text{CH}_2)_m\text{OOC}-$ are especially preferred.

- 5 Preferably, the cross-linkable group R^1 signifies $\text{CH}_2=\text{CH}-\text{COO}-$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-$, $\text{CH}_2=\text{C}(\text{Cl})-\text{COO}-$, $\text{CH}_2=\text{C}(\text{Ph})-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{COO}-\text{Ph}$, $\text{CH}_2=\text{CH}-\text{CONH}-$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-$, $\text{CH}_2=\text{C}(\text{Ph})-\text{CONH}-$, $\text{CH}_2=\text{CH}-\text{O}-$, $\text{CH}_2=\text{CH}-\text{OOC}-$, cis,trans $-\text{HOO}-\text{CR}'=\text{CR}'-\text{COO}-$,



wherein R' and R'' have the significance given above.

- These are the residues which can be cross-linked
 15 photochemically after orientation of the compounds of formula I in a field.

Especially preferred groups R^1 are $\text{CH}_2=\text{CH}-\text{COO}-$,
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{O}-$ and $\text{H}_2\text{C}-\text{CH}-$
 $\quad \quad \quad \text{O}$

20

The terms used above will be explained hereinafter:

- "1,4-phenylene optionally substituted with halogen, methyl and/or cyano" embraces in the present invention 1,4-phenylene
 25 and 1,4-phenylene mono- or multiply-substituted with fluorine, bromine, chlorine, methyl or cyano such as, for example, 2- or 3-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene, 2,6- or 3,5-difluoro-1,4-phenylene, 2- or 3-chloro-1,4-phenylene, 2,3-dichloro-1,4-phenylene, 2,6- or 3,5-dichloro-1,4-phenylene, 2-
 30 or 3-bromo-1,4-phenylene, 2- or 3-methyl-1,4-phenylene, 2- or 3-cyano-1,4-phenylene and the like;

"halogen" signifies fluorine, chlorine or bromine, especially fluorine;

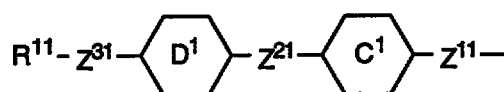
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"lower alkyl" signifies a straight-chain or branched alkyl group with 1 to 4 carbon atoms such as, for example, methyl,

ethyl, propyl, butyl, i-propyl, i-butyl, tert.-butyl, but especially methyl, ethyl, propyl or butyl.

The mesophase type of the compounds in accordance with the invention can be influenced by varying the rings in the side-chains A¹ and A². Thus, aromatic rings such as phenylene have the tendency to produce smectic phases, while saturated rings such as trans-1,4-cyclohexylene or trans-1,3-dioxane-2,5-diyl rings promote nematic tendencies.

Preferably, the mesogenic residues A¹ and A² signify a residue of formula II in which n is 1, i.e. a residue of formula II-a



II-a

wherein

rings C¹ and D¹ each independently signify pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene or 1,4-phenylene optionally substituted with fluorine;

Z¹¹ signifies -CH₂- or -CO-;

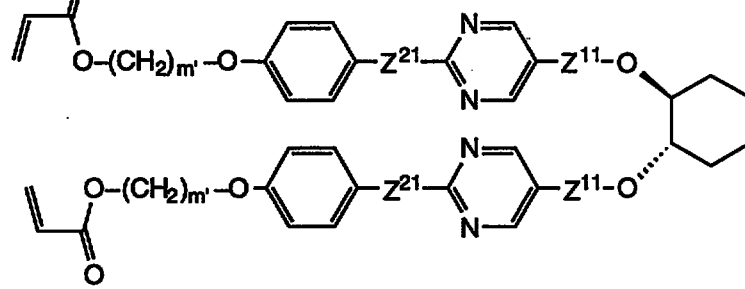
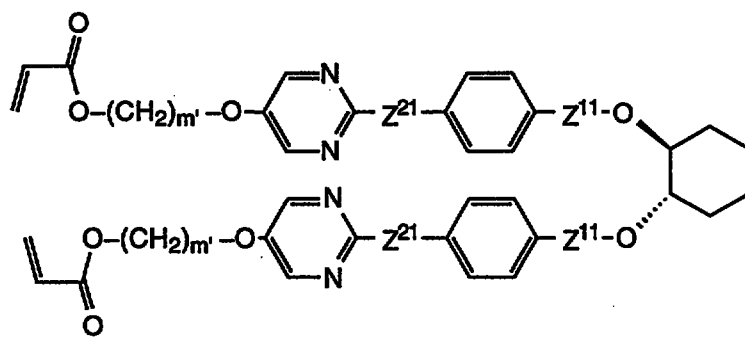
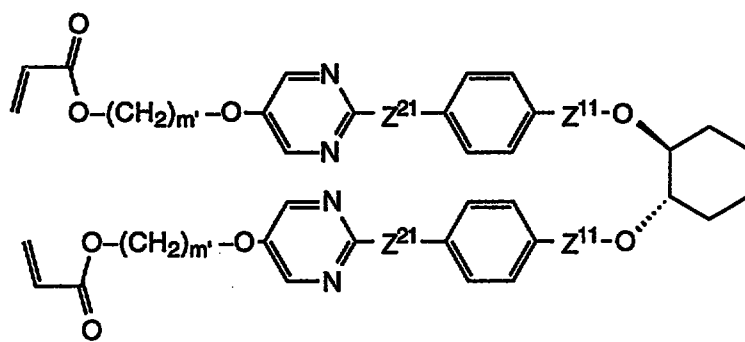
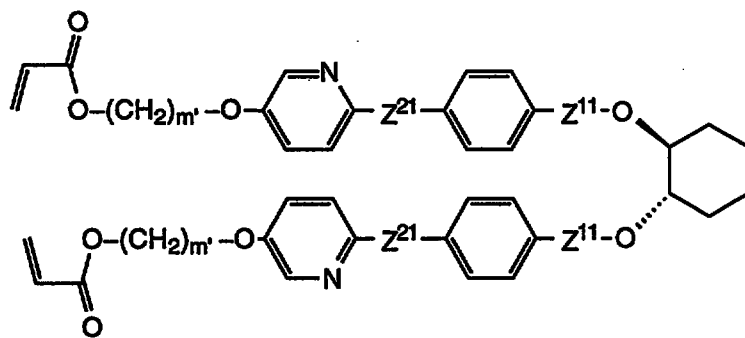
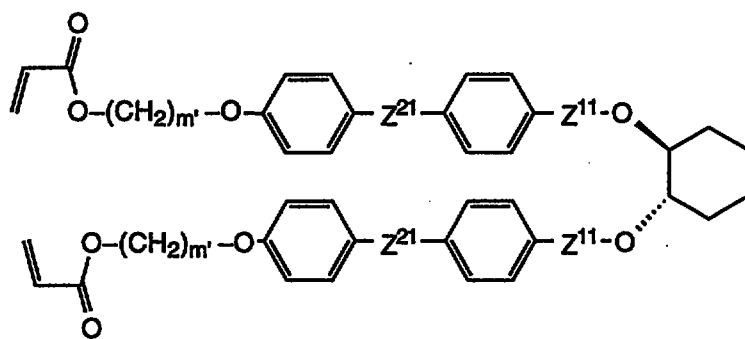
Z²¹ signifies a single bond, -CH₂O-, -COO- or -OOC-;

Z³¹ signifies -(CH₂)_{m'}-, -(CH₂)_{m'}O-, -(CH₂)_{m'}COO- or -(CH₂)_{m'}OOC-;

m' signifies a whole number of 3 to 12; and

R¹¹ signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-, CH₂=CH-O- or $\text{H}_2\text{C}-\underset{\text{O}}{\text{CH}}-$.

Especially preferred are compounds of the formulae



wherein Z^{11} signifies $-CO-$ and Z^{21} signifies a single bond or $-COO-$, especially $-COO-$, and m' is a whole number of 3 to 12,

as well as the enantiomers of these compounds.

5

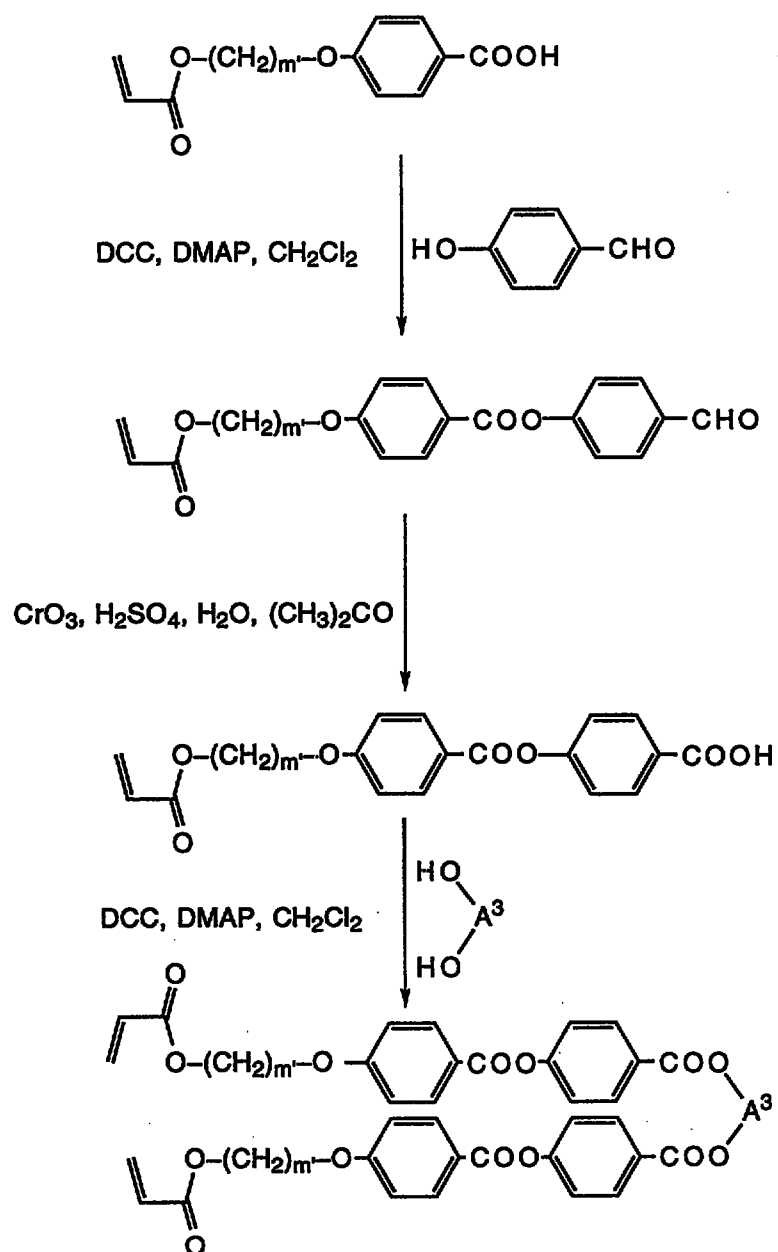
The compounds of formula I in which A^1 and A^2 have the same significance are very readily accessible synthetically and can be produced, for example, analogously to the methods illustrated in Schemes 1 to 5. Thus, optically active diols can be
10 reacted with (ω -acryloyloxyalkyloxy)-substituted carboxylic acids in a manner known per se. This esterification can be effected, for example, via the corresponding methylsulphonate in tetrahydrofuran or in the presence of N,N' -dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine in dichloromethane or
15 another suitable solvent such as e.g. chloroform. Optically active diols can also be reacted with (ω -acryloyloxyalkyloxy)-substituted benzyl tosylates in a Williamson etherification. This etherification can be effected, for example, at room temperature in the presence of potassium tert.-butylate in dimethoxyethane or
20 another suitable solvent such as e.g. N,N' -dimethylformamide.

Compounds of formula I in which A^1 and A^2 are different can be produced by the mono-esterification of optically active diols with an (ω -acryloyloxyalkyloxy)-substituted carboxylic acid
25 and subsequent esterification with a different (ω -acryloyloxyalkyloxy)-substituted carboxylic acid. The corresponding asymmetric diethers are accessible via a similar two-stage process (described). The starting materials are known and in part are commercially available.

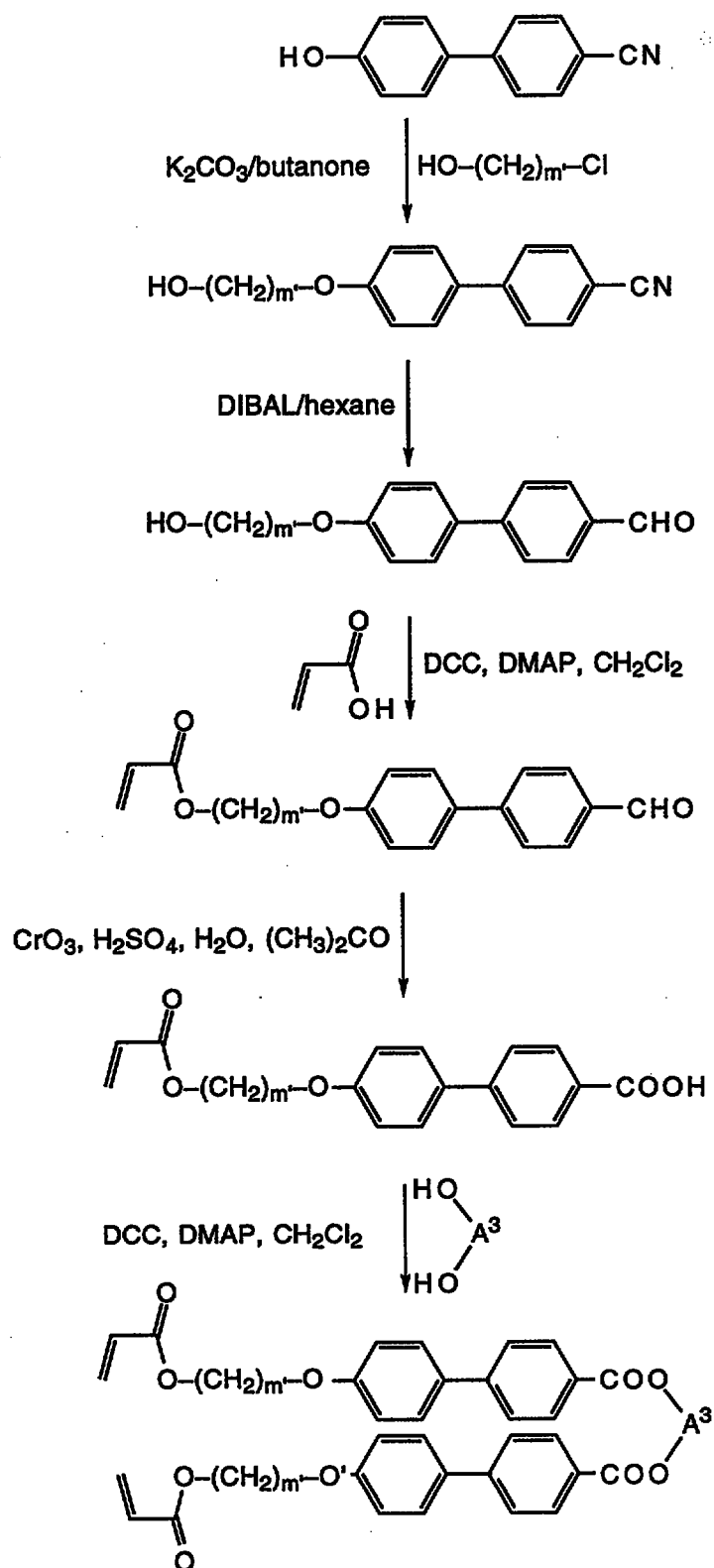
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The reactions set forth in Schemes 1 to 5 are all effected in a manner known per se. In the Schemes the symbols have the aforementioned significances.

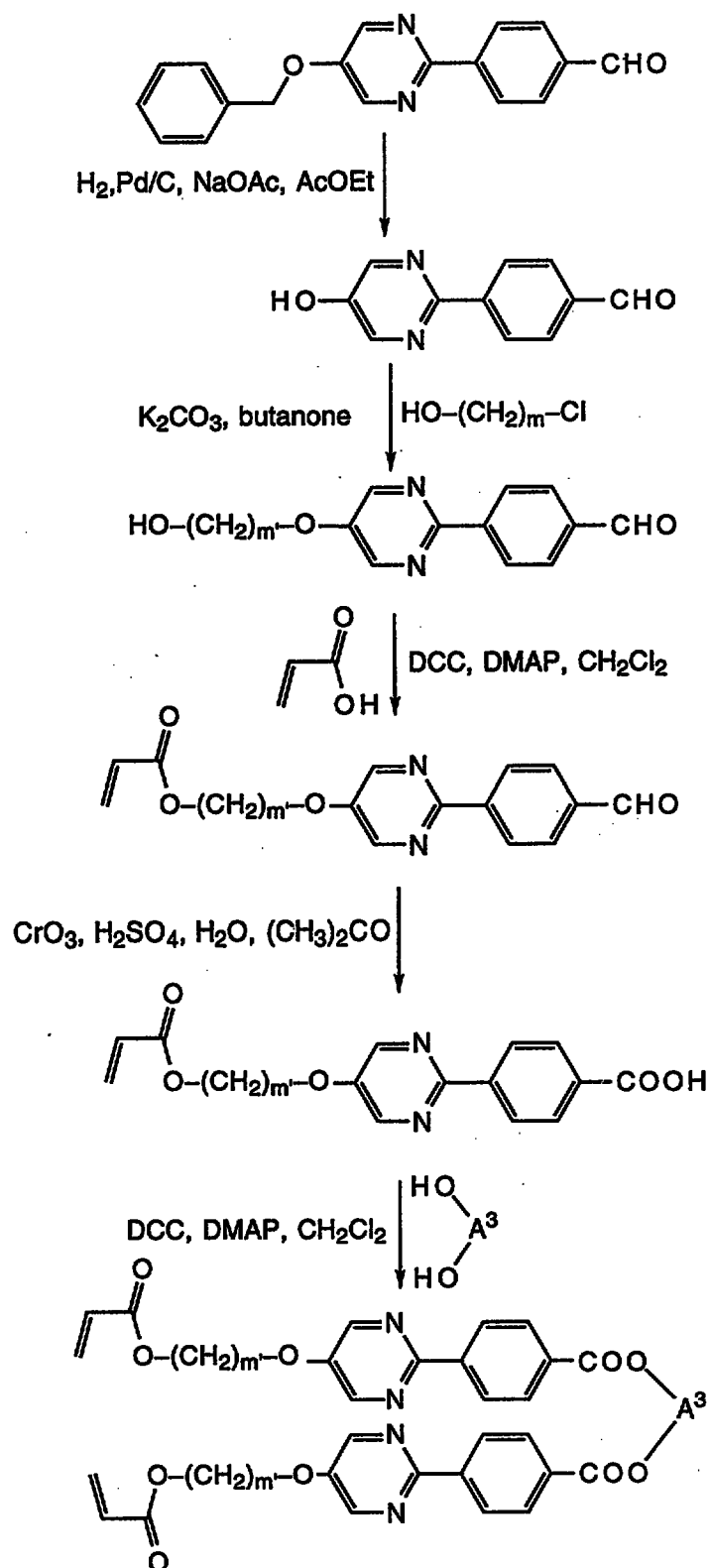
Scheme 1



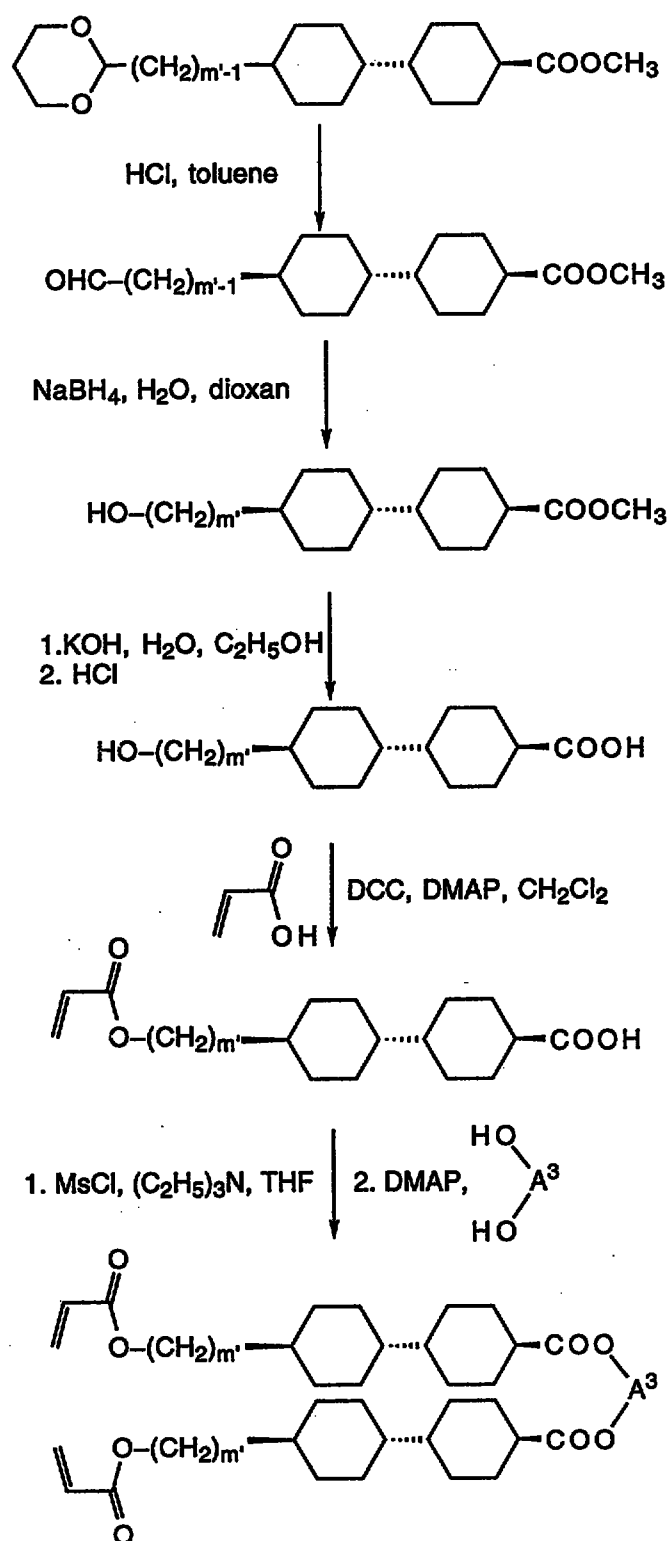
Scheme 2



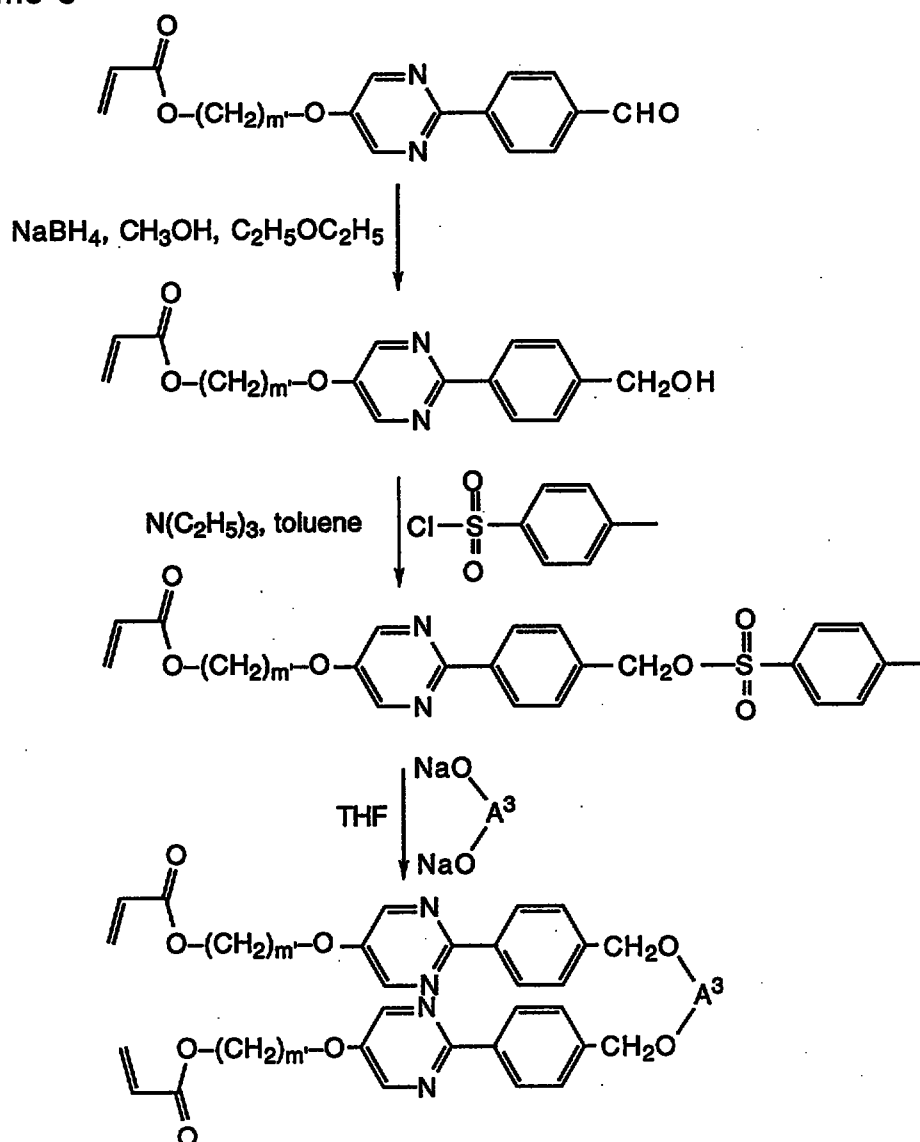
Scheme 3



Scheme 4



Scheme 5



A small amount of BHT (2,6-di-tert.-butyl-4-methyl-phenol/"butylhydroxytoluene") is admixed in each step in order to stop undesired thermal cross-linkage.

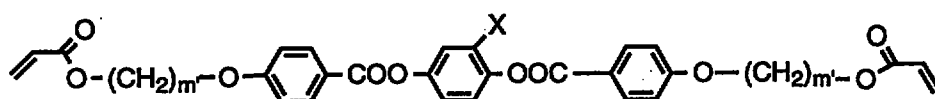
The compounds of formula I are used as chiral dopants in liquid crystalline mixtures. These liquid crystalline mixtures contain at least one compound of formula I.

The content of chiral compounds of formula I in the liquid crystalline mixtures in accordance with the invention can vary in a wide range and can be, for example, about 0.1-30 wt.% and is determined essentially by the twisting capacity of the compounds and the desired pitch.

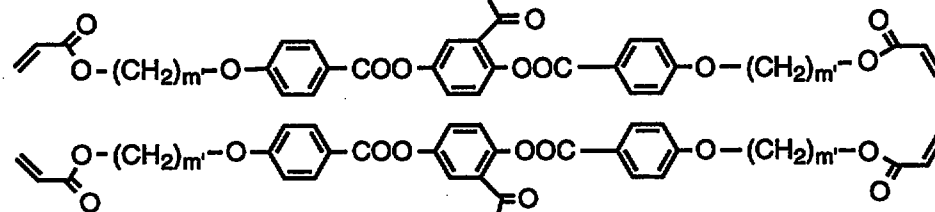
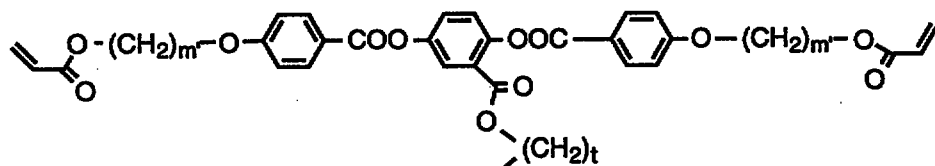
The liquid crystalline mixtures in accordance with the invention contain at least 2 components, of which at least one component is a compound of formula I. A second component and any additional components can be further compounds of formula I or other known liquid crystalline compounds having a photo cross-linkable group. Additional chiral components can also be present in the mixture.

The mixtures in accordance with the invention preferably contain, in addition to one or more compounds of formula I, one or more compounds from the group of compounds of the general formulae

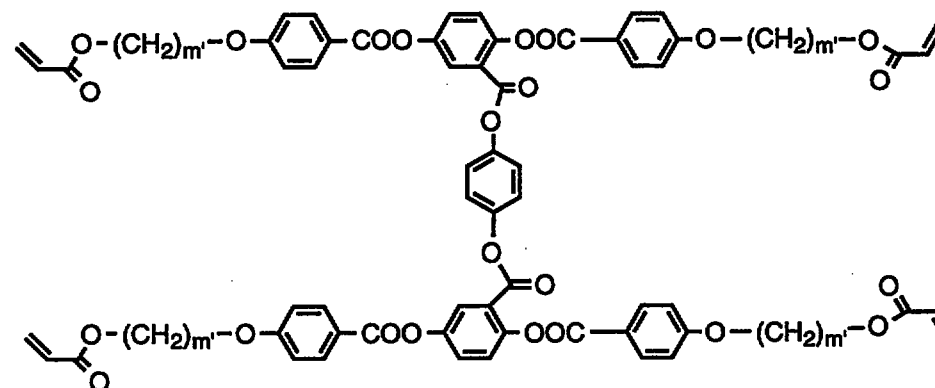
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III

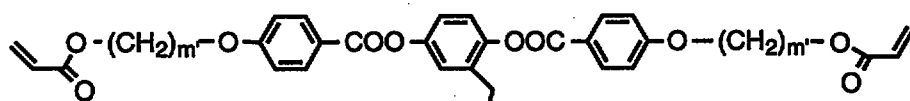


IV

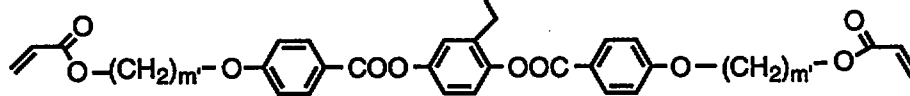


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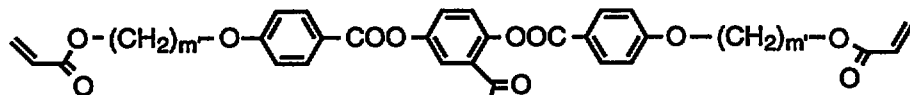
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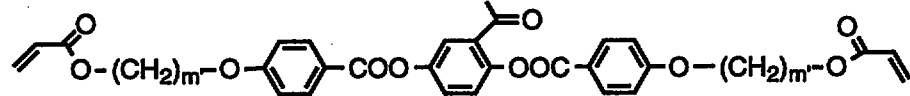
VI



VII



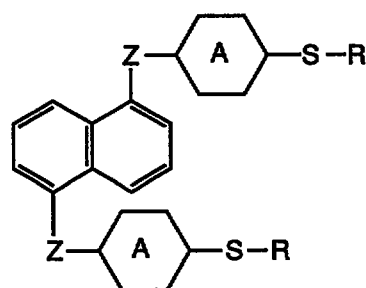
VIII



IX

5

and



X

10

X

signifies hydrogen, fluorine, chlorine, bromine or methyl;

m'

signifies a whole number of 4 to 12;

- t signifies a whole number of 2 to 12;
 Z signifies -OCH₂- or -OOC-;
 A signifies 1,4-phenylene or 2- or 3-fluoro-1,4-phenylene;
 5 S signifies -(CH₂)_m-, -(CH₂)_mO- or -O(CH₂)_m-;
 and
 R signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-,
 CH₂=CH-O- or $\begin{matrix} \text{H}_2\text{C} & \text{CH-} \\ & \diagdown \quad \diagup \\ & \text{O} \end{matrix}$.

10 The production of the compounds of formula I and of liquid crystalline mixtures containing these compounds is illustrated in more detail by the following Examples. C signifies a crystalline phase, S signifies a smectic phase, N signifies a nematic phase and I signifies the isotropic phase. Optical antipodes have in each
 15 case "mirror image properties", i.e. the same melting point etc., but lead to opposite helical rotation and opposite circular polarisation of reflected light.

Example 1

20

0.44 g of N,N'-dicyclohexylcarbodiimide was added with 5 minutes while stirring to a solution of 0.1 g of (1R,2R)-trans-1,2-cyclohexanediol, 0.9 g of 4-(4-[8-acryloyloxyoctyloxy]-phenylcarbonyloxy)benzoic acid and 0.05 g of 4-(dimethylamino)-
 25 pyridine in 20 ml of dichloromethane. The reaction mixture was stirred overnight, filtered and the filtrate was concentrated. Chromatography of the residue on silica gel with hexane/ethyl acetate (vol. 8:2) and recrystallization from ethyl alcohol of the fractions which were pure according to thin-layer chroma-
 30 tography gave 0.1 g of (1R,2R)-trans-1,2-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane; m.p. (C-I) 97°C.

The following compounds can be prepared in an analogous
 35 manner:

(1R,2R)-trans-1,2-bis[4-(5-[4-Acryloyloxybutyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane; m.p. (C-I) 107°C;

(1R,2R)-trans-1,2-bis[2-(4-[4-acryloyloxybutyloxy]-phenyl)pyridin-5-yl]carbonyloxy]cyclohexane; m.p. (C-I) 108°C;

(1R,2R)-trans-1,2-bis[4-(4-[6-acryloyloxyhexyloxy]-phenyl)cyclohexyl-ethylcarbonyloxy]cyclohexane; m.p. (C-I) 54°C.

5

There can also be prepared:

(1R,2R)-trans-1,2-bis[4-(4-[3-Acryloyloxypropyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

10 (1R,2R)-trans-1,2-bis[4-(4-[4-acryloyloxybutoxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

(1R,2R)-trans-1,2-bis[4-(4-[5-acryloyloxypentyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

15 (1R,2R)-trans-1,2-bis[4-(4-[6-acryloyloxyhexyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

(1R,2R)-trans-1,2-bis[4-(4-[7-acryloyloxyheptyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

(1R,2R)-trans-1,2-bis[4-(4-[9-acryloyloxynonyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

20 (1R,2R)-trans-1,2-bis[4-(4-[10-acryloyloxydecyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

(1R,2R)-trans-1,2-bis[4-(4-[11-acryloyloxyundecyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

25 (1R,2R)-trans-1,2-bis[4-(4-[12-acryloyloxydodecyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]cyclohexane;

(1R,2R)-trans-1,2-bis(4-[3-acryloyloxypropyloxy]biphenyl-4'-carbonyloxy)cyclohexane;

(1R,2R)-trans-1,2-bis(4-[4-acryloyloxybutoxy]biphenyl-4'-carbonyloxy)cyclohexane;

30 (1R,2R)-trans-1,2-bis(4-[5-acryloyloxypentyloxy]biphenyl-4'-carbonyloxy)cyclohexane;

(1R,2R)-trans-1,2-bis(4-[6-acryloyloxyhexyloxy]biphenyl-4'-carbonyloxy)cyclohexane;

35 (1R,2R)-trans-1,2-bis(4-[7-acryloyloxyheptyloxy]biphenyl-4'-carbonyloxy)cyclohexane;

(1R,2R)-trans-1,2-bis(4-[8-acryloyloxyoctyloxy]biphenyl-4'-carbonyloxy)cyclohexane;

- (1R,2R)-trans-1,2-bis(4-[9-acryloyloxynonyloxy]biphenyl-4'-carbonyloxy)cyclohexane;
- (1R,2R)-trans-1,2-bis(4-[10-acryloyloxydecyloxy]biphenyl-4'-carbonyloxy)cyclohexane;
- 5 (1R,2R)-trans-1,2-bis(4-[11-acryloyloxyundecyloxy]biphenyl-4'-carbonyloxy)cyclohexane;
- (1R,2R)-trans-1,2-bis(4-[12-acryloyloxydodecyloxy]biphenyl-4'-carbonyloxy)cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[3-acryloyloxypropyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- 10 (1R,2R)-trans-1,2-bis[4-(5-[5-acryloyloxypentyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[6-acryloyloxyhexyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- 15 (1R,2R)-trans-1,2-bis[4-(5-[7-acryloyloxyheptyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[8-acryloyloxyoctyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[9-acryloyloxynonyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- 20 (1R,2R)-trans-1,2-bis[4-(5-[10-acryloyloxydecyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[11-acryloyloxyundecyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- 25 (1R,2R)-trans-1,2-bis[4-(5-[12-acryloyloxydodecyloxy]-pyrimidin-2-yl)phenylcarbonyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[3-acryloyloxypropyloxy]-pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[4-acryloyloxybutyloxy]pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
- 30 (1R,2R)-trans-1,2-bis[4-(5-[5-acryloyloxypentyloxy]-pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[6-acryloyloxyhexyloxy]pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
- 35 (1R,2R)-trans-1,2-bis[4-(5-[7-acryloyloxyheptyloxy]-pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[8-acryloyloxyoctyloxy]pyridin-2-yl)phenylcarbonyloxy]cyclohexane;

- (1R,2R)-trans-1,2-bis[4-(5-[9-acryloyloxy-nonyloxy]pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
 (1R,2R)-trans-1,2-bis[4-(5-[10-acryloyloxy-decyloxy]-pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
 5 (1R,2R)-trans-1,2-bis[4-(5-[11-acryloyloxy-undecyloxy]-pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
 (1R,2R)-trans-1,2-bis[4-(5-[12-acryloyloxy-dodecyloxy]-pyridin-2-yl)phenylcarbonyloxy]cyclohexane;
 (1R,2R)-trans-1,2-bis[2-(4-[8-acryloyloxy-octyloxy]phenyl)-pyrimidin-5-ylcarbonyloxy]cyclohexane;
 10 (1R,2R)-trans-1,2-bis[2-(4-[8-acryloyloxy-octyloxy]phenyl)-pyridin-5-ylcarbonyloxy]cyclohexane;
 (1R,2R)-trans-1,2-bis[trans-4-(trans-4-[3-acryloyloxy-propyl]cyclohexyl)cyclohexanecarbonyloxy]cyclohexane;
 15 (1R,2R)-trans-1,2-bis[trans-4-(2-[trans-4-(3-acryloyloxy-propyl)cyclohexyl]ethyl)cyclohexanecarbonyloxy]cyclohexane;
 (1R,2R)-trans-1,2-bis[4-(trans-4-[3-acryloyloxy-propyl]-cyclohexyl)phenylcarbonyloxy]cyclohexane;
 (1R,2R)-trans-1,2-bis[4-(2-[trans-4-(3-acryloyloxy-propyl)cyclohexyl]ethyl)phenylcarbonyloxy]cyclohexane.
 20

Example 2

- A solution of 0.2 g of (1R,2R)-trans-1,2-cyclohexanediol,
 25 0.5 g of sodium hydride and 50 ml of tetrahydrofuran is stirred for 7 hours, treated with 1.1 g of 4-(5-[8-acryloyloxy-octyloxy]pyrimidin-2-yl)benzyl tosylate, the mixture is stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of diethyl ether each
 30 time. The organic phases are combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate is concentrated. Chromatographic purification of the residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2) and two-fold recrystallization from a
 35 cyclohexane/ethyl acetate mixture (vol. 8:2) of the fractions which are pure according to thin-layer chromatography gives 1.1 g of (1R,2R)-trans-1,2-bis[4-(5-[8-acryloyloxy-octyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane.

The following compounds can be prepared in an analogous manner:

- 5 (1R,2R)-trans-1,2-bis[4-(4-[3-Acryloyloxypropyloxy]-phenylcarbonyloxy)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(4-[4-acryloyloxybutoxy]phenylcarbonyloxy)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(4-[5-acryloyloxypentyloxy]-phenylcarbonyloxy)benzyloxy]cyclohexane;
- 10 (1R,2R)-trans-1,2-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(4-[7-acryloyloxyheptyloxy]-phenylcarbonyloxy)benzyloxy]cyclohexane;
- 15 (1R,2R)-trans-1,2-bis[4-(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(4-[10-acryloyloxydecyloxy]-phenylcarbonyloxy)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(4-[11-acryloyloxyundecyloxy]-phenylcarbonyloxy)benzyloxy]cyclohexane;
- 20 (1R,2R)-trans-1,2-bis[4-(4-[12-acryloyloxydodecyloxy]-phenylcarbonyloxy)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis(4-[3-acryloyloxypropyloxy]biphenyl-4'-methoxy)cyclohexane;
- 25 (1R,2R)-trans-1,2-bis(4-[4-acryloyloxybutoxy]biphenyl-4'-methoxy)cyclohexane;
- (1R,2R)-trans-1,2-bis(4-[5-acryloyloxypentyloxy]biphenyl-4'-methoxy)cyclohexane;
- (1R,2R)-trans-1,2-bis(4-[6-acryloyloxyhexyloxy]biphenyl-4'-methoxy)cyclohexane;
- 30 (1R,2R)-trans-1,2-bis(4-[7-acryloyloxyheptyloxy]biphenyl-4'-methoxy)cyclohexane;
- (1R,2R)-trans-1,2-bis(4-[9-acryloyloxynonyloxy]biphenyl-4'-methoxy)cyclohexane;
- 35 (1R,2R)-trans-1,2-bis(4-[10-acryloyloxydecyloxy]biphenyl-4'-methoxy)cyclohexane;
- (1R,2R)-trans-1,2-bis(4-[11-acryloyloxyundecyloxy]biphenyl-4'-methoxy)cyclohexane;

- (1R,2R)-trans-1,2-bis(4-[12-acryloyloxydodecyloxy]-biphenyl-4'-methoxy)cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[3-acryloyloxypropyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- 5 (1R,2R)-trans-1,2-bis[4-(5-[4-acryloyloxybutyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[5-acryloyloxypentyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[6-acryloyloxyhexyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- 10 (1R,2R)-trans-1,2-bis[4-(5-[7-acryloyloxyheptyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[8-acryloyloxyoctyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- 15 (1R,2R)-trans-1,2-bis[4-(5-[9-acryloyloxynonyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[10-acryloyloxydecyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[11-acryloyloxyundecyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- 20 (1R,2R)-trans-1,2-bis[4-(5-[12-acryloyloxydodecyloxy]-pyrimidin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[3-acryloyloxypropyloxy]-pyridin-2-yl)benzyloxy]cyclohexane;
- 25 (1R,2R)-trans-1,2-bis[4-(5-[4-acryloyloxybutyloxy]pyridin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[5-acryloyloxypentyloxy]-pyridin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[6-acryloyloxyhexyloxy]pyridin-2-yl)benzyloxy]cyclohexane;
- 30 (1R,2R)-trans-1,2-bis[4-(5-[7-acryloyloxyheptyloxy]-pyridin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[8-acryloyloxyoctyloxy]pyridin-2-yl)benzyloxy]cyclohexane;
- 35 (1R,2R)-trans-1,2-bis[4-(5-[9-acryloyloxynonyloxy]pyridin-2-yl)benzyloxy]cyclohexane;
- (1R,2R)-trans-1,2-bis[4-(5-[10-acryloyloxydecyloxy]-pyridin-2-yl)benzyloxy]cyclohexane;

(1R,2R)-trans-1,2-bis[4-(5-[11-acryloyloxyundecyloxy]-pyridin-2-yl)benzyloxy]cyclohexane;

(1R,2R)-trans-1,2-bis[4-(5-[12-acryloyloxydodecyloxy]-pyridin-2-yl)benzyloxy]cyclohexane;

5 (1R,2R)-trans-1,2-bis[(2-[4-(8-acryloyloxyoctyloxy)-phenyl]pyrimidin-5-yl)methoxy]cyclohexane;

(1R,2R)-trans-1,2-bis[(trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)cyclohexyl)methoxy]cyclohexane;

10 (1R,2R)-trans-1,2-bis[(trans-4-[2-(trans-4-[3-acryloyloxypropyl]cyclohexyl)ethyl]cyclohexyl)methoxy]cyclohexane;

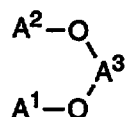
(1R,2R)-trans-1,2-bis[4-(trans-4-[3-acryloyloxypropyl]-cyclohexyl)benzyloxy]cyclohexane;

(1R,2R)-trans-1,2-bis[4-(2-[trans-4-(3-acryloyloxypropyl)cyclohexyl]ethyl)benzyloxy]cyclohexane.



Claims

1. Compounds of the general formula



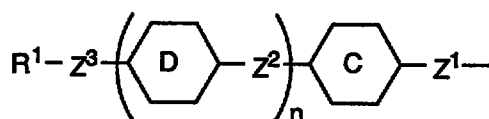
5

wherein

A¹ and A² each signify a cross-linkable mesogenic residue; and

10 A³ signifies (R,R)- or (S,S)-trans-1,2-cyclohexyl-diyl.

15 2. Compounds according to claim 1, wherein the mesogenic residues A¹ and A² each signify a residue of general formula II



II

wherein

20 rings C and D each independently signify pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or 1,4-phenylene optionally substituted with halogen, methyl and/or cyano;

25 Z¹ signifies -(CH₂)_m-, -CO-, -(CH₂)_mCO- or -(CH₂)_mOOC-;

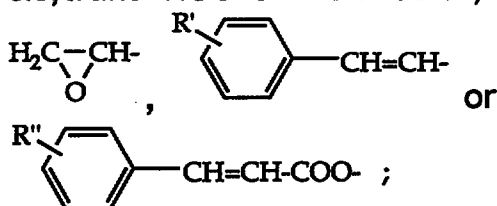
Z² signifies a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;

30 Z³ -(CY₂)_m-, -O(CY₂)_m-, -(CY₂)_mO-, -(CY₂)_mCOO-, -(CY₂)_mOOC-, -[Si[(CH₃)₂]O]_m-, -OCH₂[Si[(CH₃)₂]O]_m-, -Si[(CH₃)₂]CH₂O- or -NHCH₂[Si[(CH₃)₂]O]_m-, -Si[(CH₃)₂]CH₂NH-;

35 Y signifies hydrogen or fluorine;

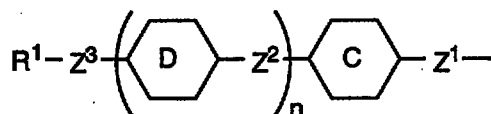


n signifies 0, 1 or 2;
 m signifies a whole number of 1 to 16; and
 R¹ signifies a cross-linkable group of the
 structure CH₂=CH-, CH₂=CH-COO-,
 CH₂=C(CH₃)-COO-, CH₂=C(Cl)-COO-,
 CH₂=C(Ph)-COO-, CH₂=CH-COO-Ph-,
 CH₂=CH-CO-NH-, CH₂=C(CH₃)-CONH-,
 CH₂=C(Cl)-CONH-, CH₂=C(Ph)-CONH-,
 CH₂=C(COOR')-CH₂-COO-, CH₂=CH-O-,
 CH₂=CH-OOC-, Ph-CH=CH-, CH₃-C(=NR')-,
 cis,trans HOO-CR'=CR'-COO-,



Ph signifies phenyl;
 R' signifies lower alkyl; and
 R'' signifies methyl, methoxy, cyano or halogen;
 with the proviso that R¹-Z³ contains no -O-O- or -N-O- groups.

3. Compounds according to claim 1 or 2, wherein the mesogenic residues A¹ and A² each signify a residue of general formula II



wherein
 rings C and D

each independently signify pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or 1,4-phenylene optionally substituted with halogen, methyl and/or cyano;
 Z¹ signifies -CH₂-, -CO-, -(CH₂)₃- or -(CH₂)₂CO-;



	Z ²	signifies a single bond, -CH ₂ CH ₂ -, -CH ₂ O-, -OCH ₂ -, -COO-, -OOC-, -(CH ₂) ₄ -, -O(CH ₂) ₃ - or -(CH ₂) ₃ O-;
5	Z ³	-(CY ₂) _m -, -O(CY ₂) _m -, -(CY ₂) _m O-, -(CY ₂) _m COO-, -(CY ₂) _m OOC-, -(Si[(CH ₃) ₂]O) _m -, -OCH ₂ (Si[(CH ₃) ₂]O) _m -Si[(CH ₃) ₂]CH ₂ O- or -NHCH ₂ (Si[(CH ₃) ₂]O) _m -Si[(CH ₃) ₂]CH ₂ NH-;
10	Y	signifies hydrogen or fluorine;
	n	signifies 0 or 1;
	m	signifies a whole number of 1 to 16; and
15	R ¹	signifies a cross-linkable group of the structure CH ₂ =CH-, CH ₂ =CH-COO-, CH ₂ =C(CH ₃)-COO-, CH ₂ =C(Cl)-COO-, CH ₂ =C(Ph)-COO-, CH ₂ =CH-COO-Ph-, CH ₂ =CH-CO-NH-, CH ₂ =C(CH ₃)-CONH-, CH ₂ =C(Cl)-CONH-, CH ₂ =C(Ph)-CONH-, CH ₂ =C(COOR')-CH ₂ -COO-, CH ₂ =CH-O-, CH ₂ =CH-OOC-, Ph-CH=CH-, CH ₃ -C(=NR')-,
20		cis,trans HOO-CR'=CR'-COO-, $\text{H}_2\text{C} \begin{array}{c} \diagup \diagdown \\ \text{O} \end{array} \text{CH}-$, $\text{R}' \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}=\text{CH}-$ or $\text{R}'' \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}=\text{CH}-\text{COO}-$
25	Ph	signifies phenyl;
	R'	signifies lower alkyl; and
	R''	signifies methyl, methoxy, cyano or halogen;

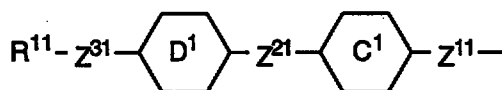
with the proviso that R¹-Z³ contains no -O-O- or -N-O- groups.

30 4. Compounds according to claim 2 or 3, wherein the mesogenic residues A¹ and A² have the same significance.

5. Compounds according to any one of claims 1 to 4, wherein the residues A¹ and A² signify a residue of formula II-a



26



II-a

wherein

rings C¹ and D¹ each independently signify pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene or 1,4-phenylene optionally substituted with fluorine;

Z¹¹ signifies -CH₂- or -CO-;

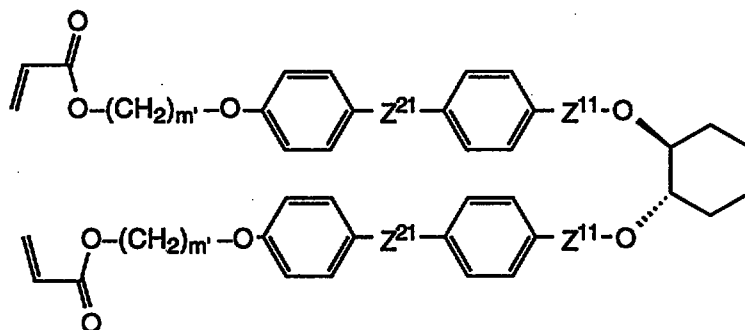
Z²¹ signifies a single bond, -CH₂O-, -COO- or -OOC-;

Z³¹ signifies -(CH₂)_{m'}-, -(CH₂)_{m'}O-, -(CH₂)_{m'}COO- or -(CH₂)_{m'}OOC-;

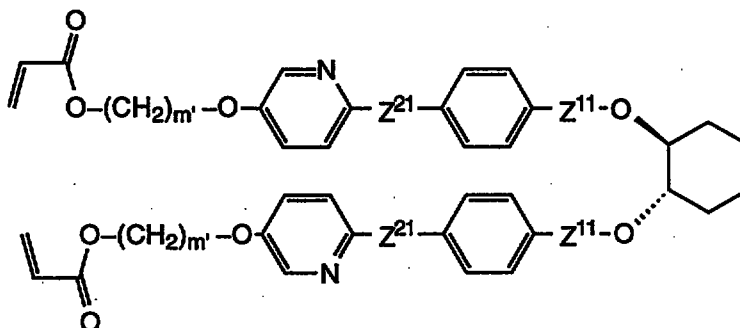
m' signifies a whole number of 3 to 12; and

R¹¹ signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-, CH₂=CH-O- or $\text{H}_2\text{C}-\underset{\text{O}}{\text{CH}}-$.

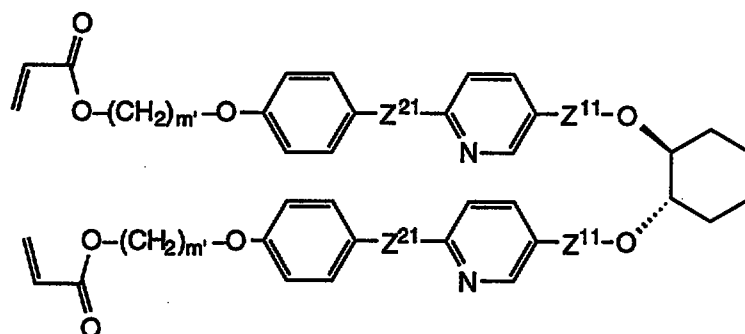
6. Compounds according to claim 5 of formulae IA-IE



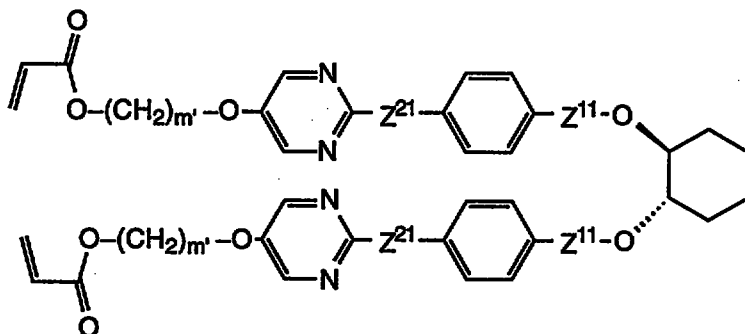
I - A



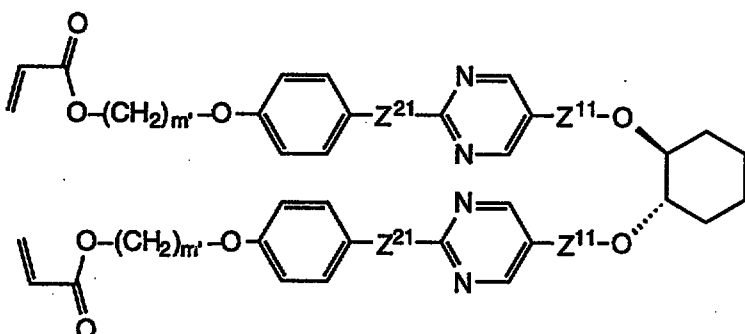
I - B



I - C



I - D



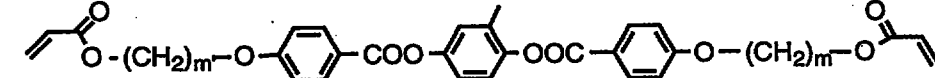
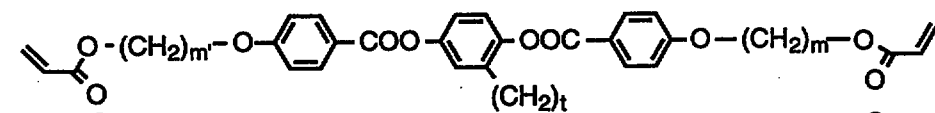
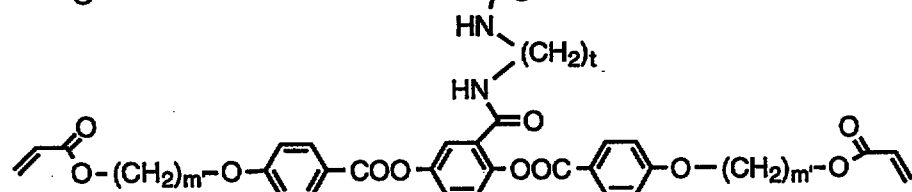
I - E

- 5 wherein Z^{11} signifies $-\text{CO}-$ and Z^{21} signifies a single bond or $-\text{COO}-$, especially $-\text{COO}-$, and m' is a whole number of 3 to 12,

as well as the enantiomers of these compounds.

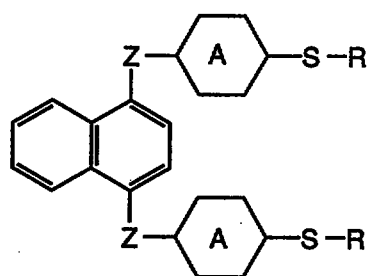
- 10 7. A cross-linkable liquid crystalline mixture consisting of at least 2 components, wherein at least one component is an optically active compound of the formula I defined in claim 1.

- 15 8. A cross-linkable liquid crystalline mixture according to claim 7, which contains, in addition to one or more compounds of formula I, one or more compound from the group of the formulae



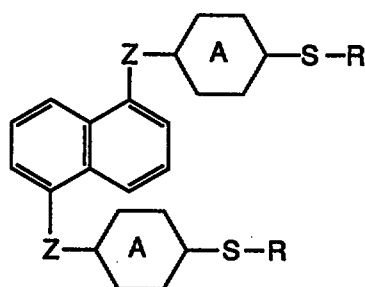


29



IX

and



X

5

wherein

X signifies hydrogen, fluorine, chlorine, bromine or methyl;

10 m' signifies a whole number of 3 to 12;

t signifies a whole number of 2 to 12;

Z signifies -OCH₂- or -OOC-;

A signifies 1,4-phenylene or 2- or 3-fluoro-1,4-phenylene;

15 S signifies -(CH₂)_{m'}-; -(CH₂)_{m'}O- or -O(CH₂)_{m'}-; and

R signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-,
CH₂=CH-O- or $\text{H}_2\text{C}-\text{CH}-\text{O}$.

20 9. The use of compounds according to any one of claims 1 to 6 in their cross-linked state for optical components.

10. The use of cross-linkable liquid crystalline mixtures according to claim 7 or 8 in their cross-linked state for optical
25 components.
