

The present invention is concerned with photo cross-
5 linkable liquid crystalline 1,4-dioxane-2,3-diyl derivatives,
liquid crystalline mixtures which contain such compounds and
their use in the cross-linked state for optical components.

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

20 Further properties such as, for example, the birefringence,
the refractive index, the transparency, etc. must fulfil different
requirements depending on the field of use. Thus, materials for
optical filters should have a strong absorption in a direction
perpendicular to the filter surface.

25 In addition to the general use of photo cross-linkable liquid
crystals for optical components, such liquid crystalline materials
are suitable as a cladding for glass fibres for optical data
transmission. The use of such materials increases the elastic
30 modulus in the longitudinal axis of the fibre, reduces the thermal
expansion coefficient and avoids microdistortion losses. This
leads to an increased mechanical stability.

The photo cross-linkable liquid crystals must have a good
35 chemical and thermal stability, good solubility in common
solvents and a good stability towards electric fields and electro-
magnetic radiation. They should have a suitable mesophase in a
temperature range of about 25°C to about +100°C, especially of
about 25°C to about +80°C. Moreover, it is important that the

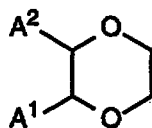


components have a good miscibility with one another, since liquid crystals are usually used as mixtures of several components. Conventional photochemically oligomerisable or polymerisable liquid crystals usually have a high melting point and clearing point. This has the disadvantage that a spontaneous, thermal polymerisation can occur prematurely during processing, which is carried out at temperatures barely below the clearing point, because at this temperature the viscosity in the liquid crystalline state is at the lowest and is therefore favourable for a good orientability. This spontaneous polymerisation leads to the formation of domains, whereby the optical and thermal properties in the cross-linked layers which are produced can be clearly influenced. The melting point can be decreased by the production of complicated mixtures having several components, which permits a processing at lower temperatures, but brings with it the danger of a crystallisation of the conventional polymerisable liquid crystals. Photochemically oligomerisable or polymerisable compounds are described, for example, in EP-A-0 331 233.

There is accordingly the need, especially for use in optical filters, to produce photochemically oligomerisable or polymerisable compounds which have relatively low melting points and clearing points in order that they can be processed very readily at temperatures above room temperature in the liquid crystalline state and also in solution. Further, they should be orientable and structurable as domain-free as possible and also should have an excellent thermal stability and long-term stability in the cross-linked state. Moreover, especially for optical retarders, mixtures having an adjustable optical isotropy should be available in order that, for example, the optical delay of an optical retarder can be adjusted. Conventional photochemically oligomerisable or polymerisable liquid crystals as described, for example, in EP-A-0 331 233 contain predominantly aromatic rings and therefore usually have a very large optical anisotropy.

The present invention now provides compounds which are suitable in an outstanding manner as single components or as

components of such liquid crystal mixtures. These are compounds of the general formula



5

wherein

A¹ and A²

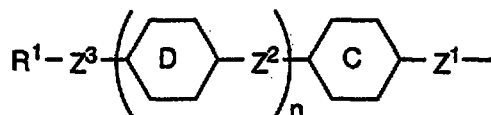
each represent a cross-linkable, mesogenic residue.

10

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

15

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



20

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;

25

Z¹

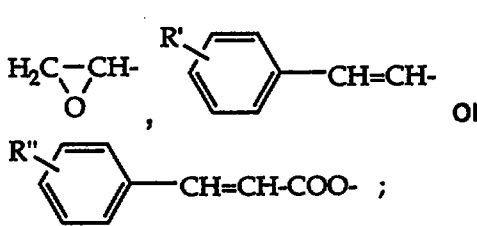
signifies -CH₂-(CH₂)_m-, -(CH₂)_mO-, -O(CH₂)_m-, -COO-, -OOC-, -(CH₂)_mCOO- or -(CH₂)_mOOC-;

Z²

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

30

- Z^3 signifies $-(CY_2)_m-$, $-O(CY_2)_m-$, $-(CY_2)_mO-$,
 $-(CY_2)_mCOO-$, $-(CY_2)_mOOC-$,
 $-(Si[(CH_3)_2]O)_m-$,
 $-OCH_2(Si[(CH_3)_2]O)_mSi[(CH_3)_2]CH_2O-$ or
 $-NHCH_2(Si[(CH_3)_2]O)_mSi[(CH_3)_2]CH_2NH-$;
 Y signifies hydrogen or fluorine;
 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 $CH_2=CH-$, $CH_2=CH-COO-$,
 $CH_2=C(CH_3)-COO-$, $CH_2=C(Cl)-COO-$,
 $CH_2=C(Ph)-COO-$, $CH_2=CH-COO-Ph-$,
 $CH_2=CH-CO-NH-$, $CH_2=C(CH_3)-CONH-$,
 $CH_2=C(Cl)-CONH-$, $CH_2=C(Ph)-CONH-$,
 $CH_2=C(COOR')-CH_2-COO-$, $CH_2=CH-O-$,
 $CH_2=CH-OOC-$, $Ph-CH=CH-$, $CH_3-C(=NR')-$,
cis,trans $HOO-CR'=CR'-COO-$,



 Ph signifies phenyl;
 R' signifies lower alkyl; and
 R'' signifies methyl, methoxy, cyano or
halogen;
- 25 with the proviso that R^1-Z^3 contains no $-O-O-$ or $-N-O-$ groups.

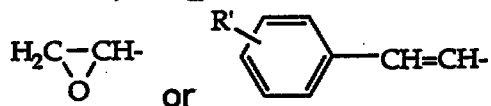
Compounds of formula I in which the two mesogenic residues A^1 and A^2 have the same significance are especially preferred.

30

Residues A^1 and A^2 of formula II in which rings C and D each independently signify pyridine-2,5-diyl, pyrimidine-2,5-diyl or 1,4-phenylene which is unsubstituted or substituted with fluorine, Z^1 signifies $-CH_2-CH_2-$, $-CH_2O-$, $-COO-$ or $-OOC-$, Z^2
35 signifies a single bond, $-CH_2CH_2-$, $-CH_2O-$, $-OCH_2-$, $-COO-$ or

-OOC- and Z³ signifies $-(CH_2)_m-$, $-(CH_2)_mO-$, $-(CH_2)_mCOO-$ or $-(CH_2)_mOOC-$ are especially preferred.

The cross-linkable group R¹ preferably signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-, CH₂=C(Cl)-COO-, CH₂=C(Ph)-COO-,
 5 CH₂=CH-COO-Ph-CH₂=CH-CONH-, CH₂=C(CH₃)-CONH-, CH₂=C(Ph)-CONH-, CH₂=CH-O-, CH₂=CH-OOC-, cis,trans -HOO-CR'=CR'-COO-,



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

It is these residues which can be cross-linked photochemically after orientation of the compounds of formula I in a field.

15

Especially preferred groups R¹ are CH₂=CH-COO-, CH₂=C(CH₃)-COO-, CH₂=CH-O- and $\begin{array}{c} \text{H}_2\text{C}-\text{CH}- \\ \quad \quad \quad \text{O} \end{array}$.

The terms used above will be explained hereinafter:

20

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

30

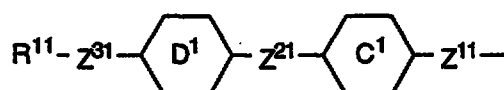
"lower alkyl" embraces straight-chain or branched residues with 1 to 5 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, i-propyl, i-butyl, t.butyl and the like;

35

"halogen" stands for fluorine, chlorine or bromine, especially for fluorine.

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 = 1, i.e. a residue of formula II-a



II-a

wherein

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

Z¹¹ signifies -CH₂CH₂-, -CH₂O-, -COO- or -OOC-;

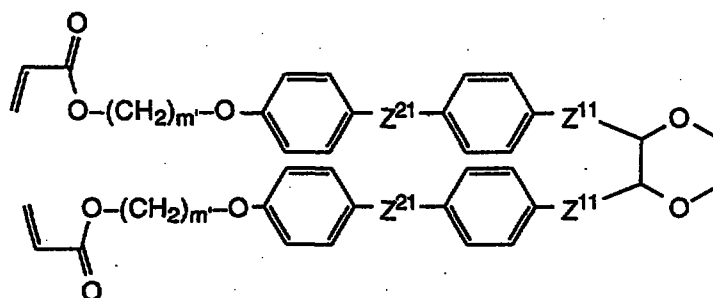
Z²¹ signifies a single bond, -CH₂O-, -COO- or -OOC-;

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

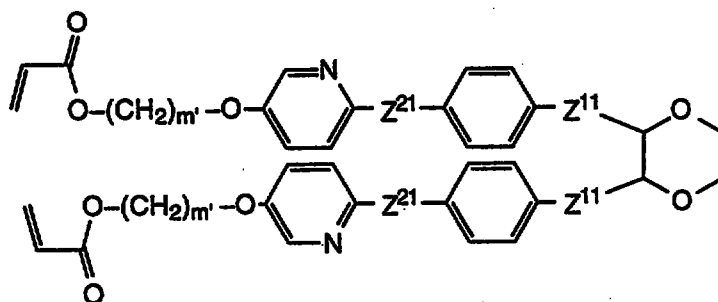
m' signifies a whole number of 3 to 12; and

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

Compounds of the formulae are particularly preferred

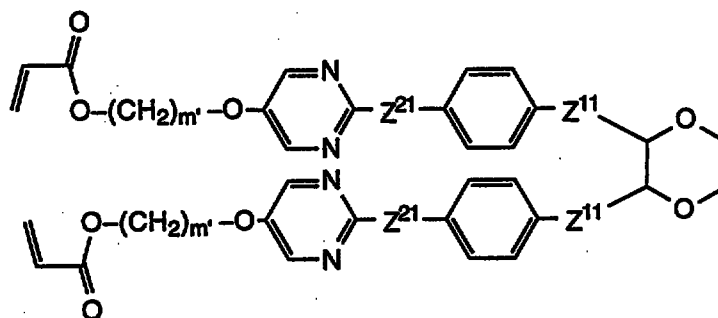


I-A



I - B

and



I - C

5

wherein

Z¹¹

signifies -COO-;

Z²¹

signifies a single bond or -COO-,
especially -COO-; and

m'

signifies a whole number of 3 to 12.

10

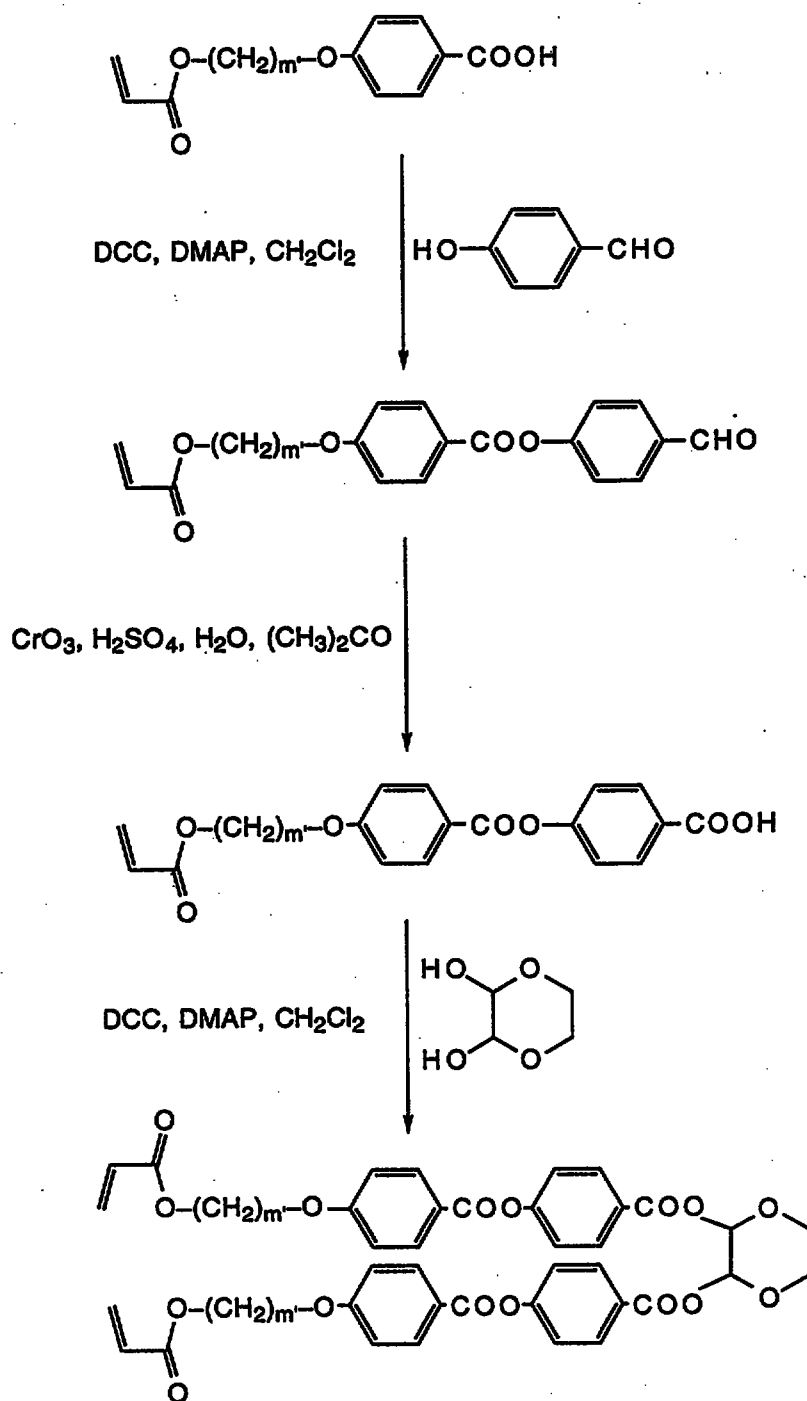
The compounds of formula I in which A¹ and A² have the same significance are very readily accessible synthetically and can be produced, for example, analogously to the methods illustrated in Schemes 1 to 5. Thus, trans-2,3-dihydroxy-1,4-dioxane can be reacted with (ω-acryloyloxyalkyloxy)-substituted 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 another suitable solvent such as e.g. chloroform. trans-2,3-Dihydroxy-1,4-dioxane can also be reacted in a Williamson etherification with (ω-acryloyloxyalkyloxy)-substituted benzyl tosylates. This esterification can be effected, for example, at room temperature in the presence of potassium tert.-butylate in dimethoxyethane or another suitable solvent

25

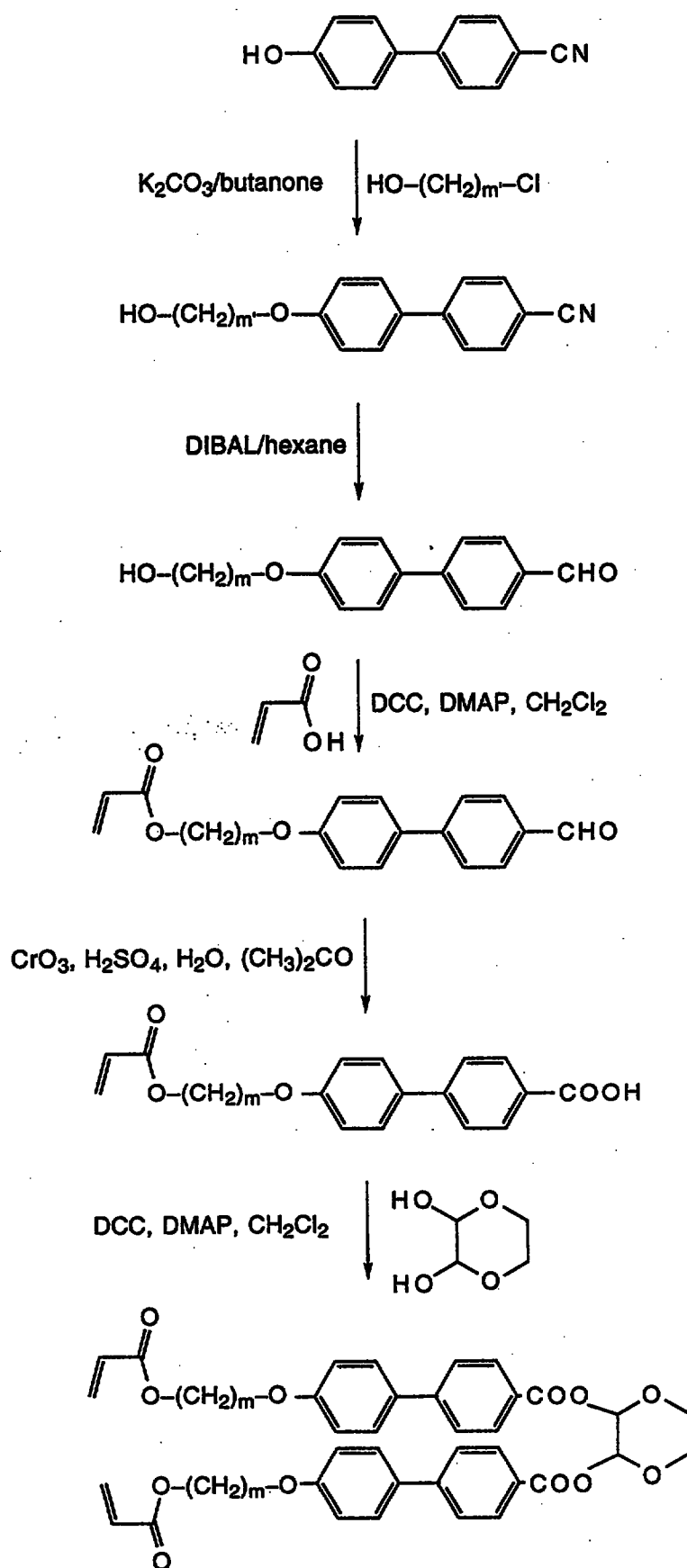
such as e.g. N,N'-dimethylformamide. trans-2,3-Dihydroxy-1,4-dioxane is commercially available.

Compounds of formula I in which A¹ and A² are different
5 can be produced by mono-esterifying trans-2,3-dihydroxy-1,4-dioxane with an (ω-acryloyloxyalkyloxy)-substituted carboxylic acid. Subsequent esterification with a different (ω-acryloyloxy-alkyloxy)-substituted carboxylic acid gives the asymmetric diester. The corresponding asymmetric diethers are accessible
10 by an analogous two-step process in which, for example, trans-2,3-dihydroxy-1,4-dioxane is firstly monoalkylated with an (ω-acryloyloxyalkyloxy)-substituted benzyl tosylate and subsequently with a different (ω-acryloyloxyalkyloxy)-substituted benzyl tosylate. The starting materials are known and are in part
15 commercially available.

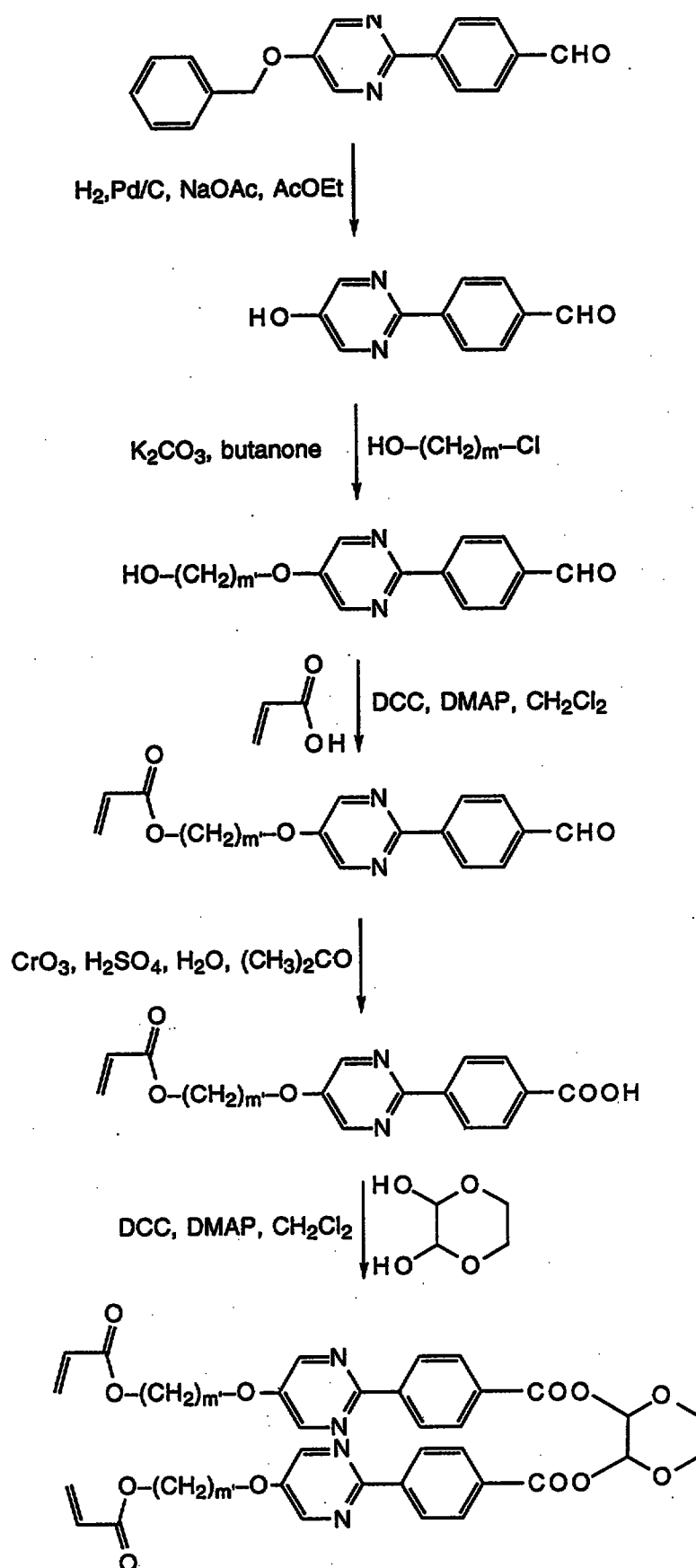
The reactions illustrated in Schemes 1 to 5 are standard methods in liquid crystal chemistry. The symbols used therein have the aforementioned significances.



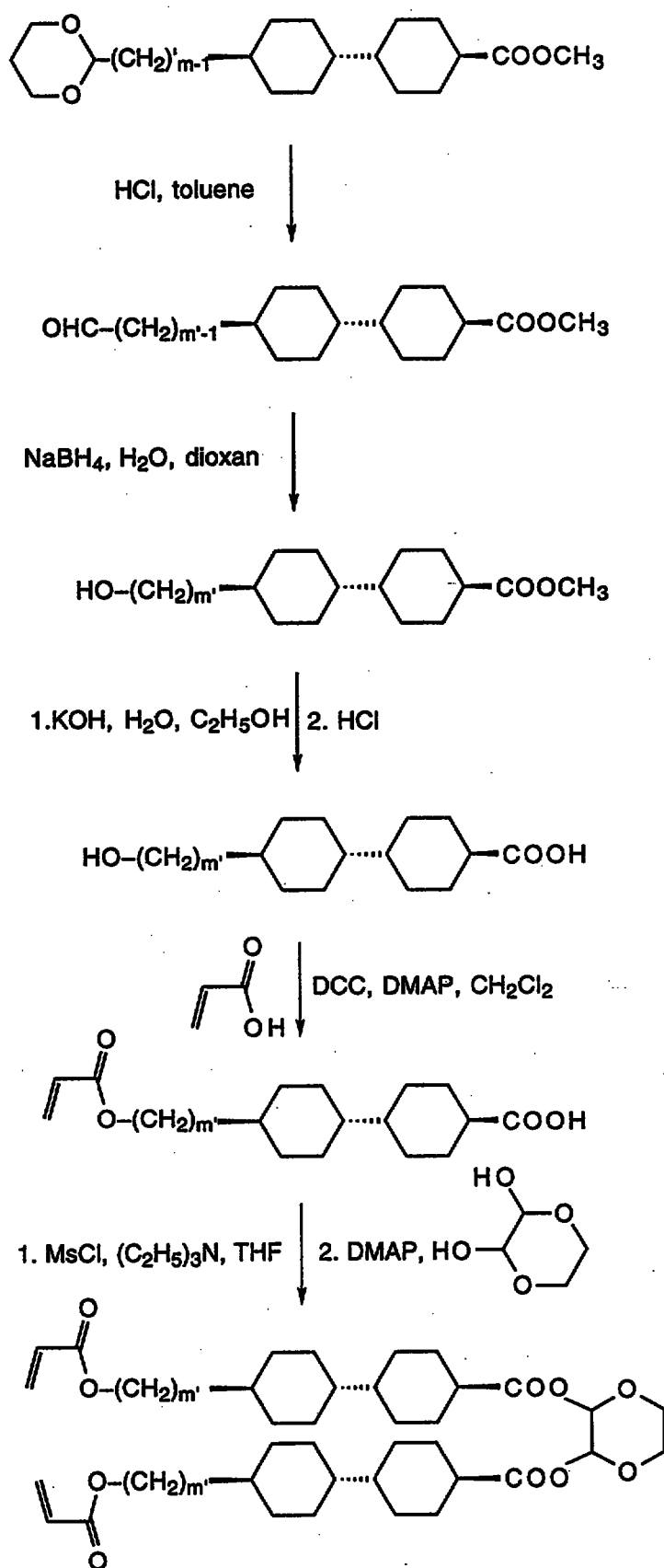
Scheme 2



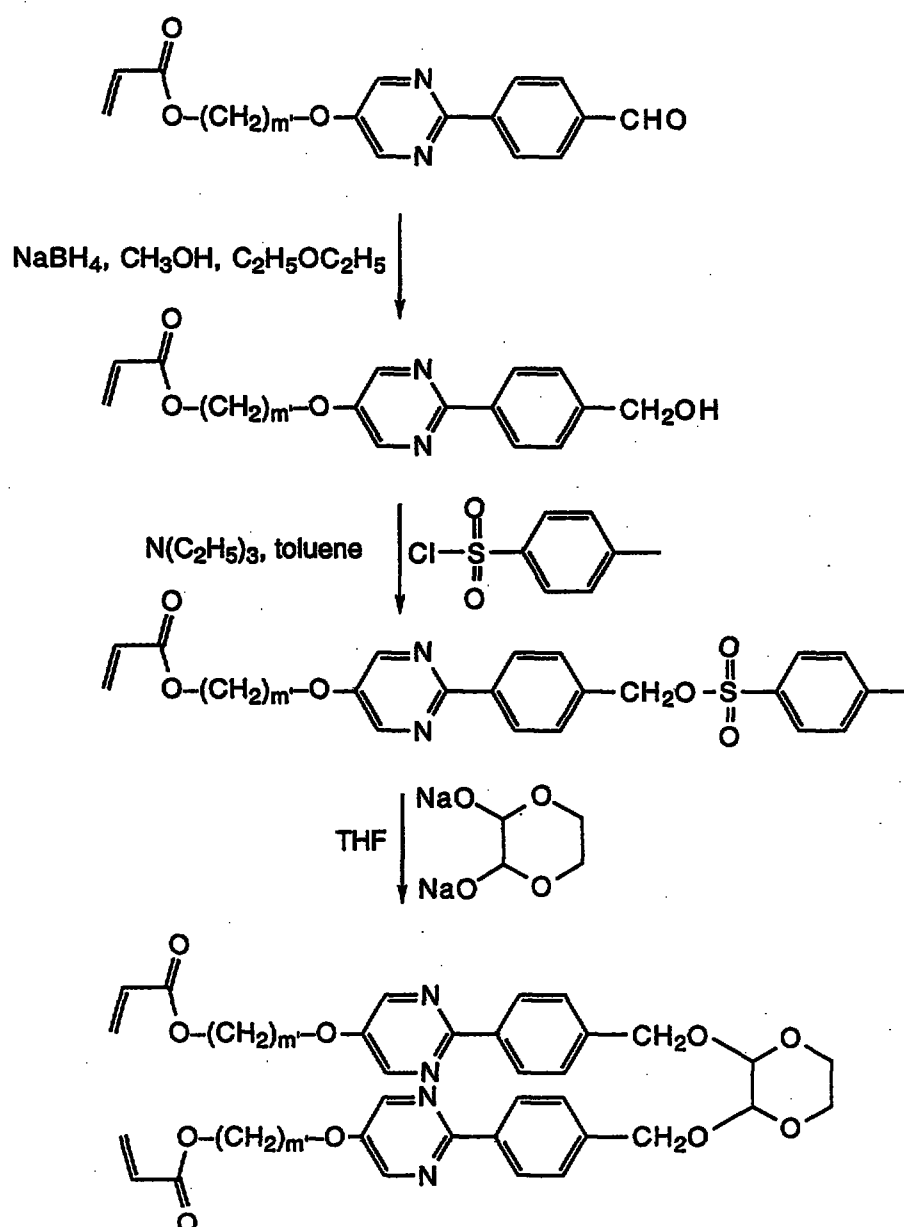
Scheme 3



Scheme 4



Scheme 5



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

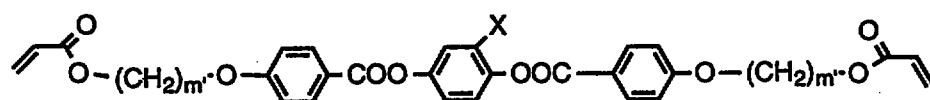
- 10 The compounds of formulae I can be used as single compounds or in the form of mixtures with one another and/or with other liquid crystal components.

The liquid crystalline mixtures in accordance with the invention contain at least 2 components, of which at least one

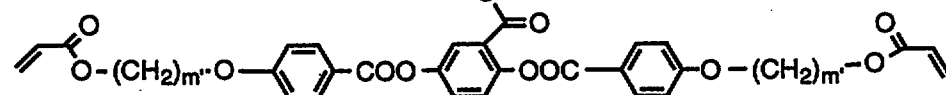
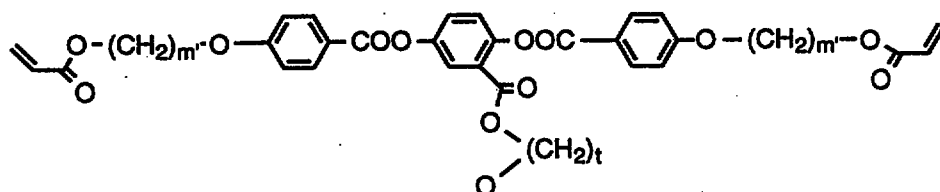
component is a compound of formula I. A second component and any other components can be additional compounds of formula I or other known liquid crystalline compounds having a photo cross-linkable group. One or more chiral components can also be present in the mixture.

Having regard to the good solubility of the compounds of formula I and having regard to their good miscibility with one another, the content of compounds of formula I in the mixtures in accordance with the invention can be high and can amount to 100 wt.%.
 10

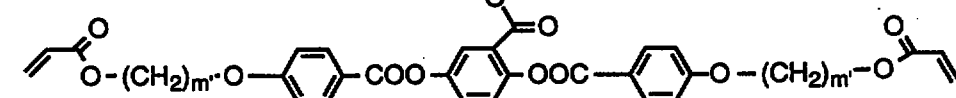
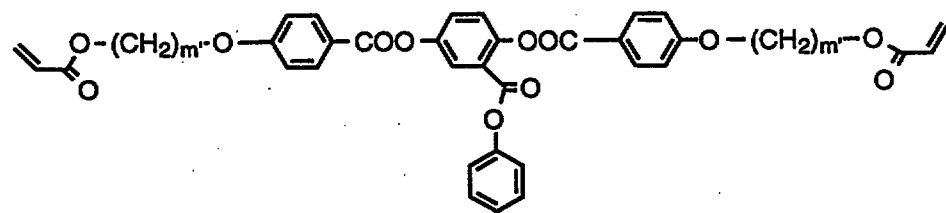
The mixtures in accordance with the invention preferably contain, in addition to one or more compounds of formula I, one or more compounds from the group of compounds of the general formulae
 15



III

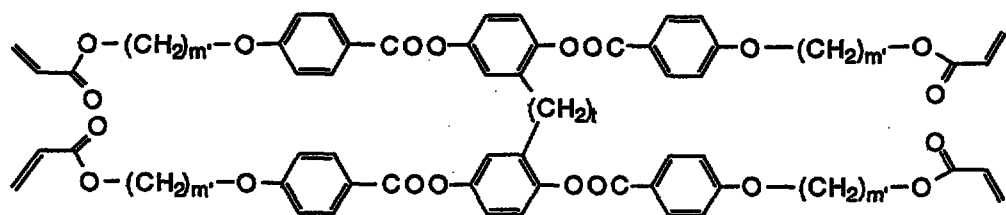
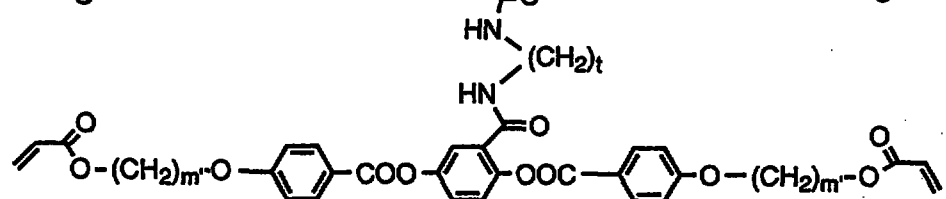
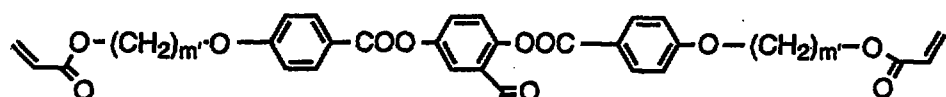
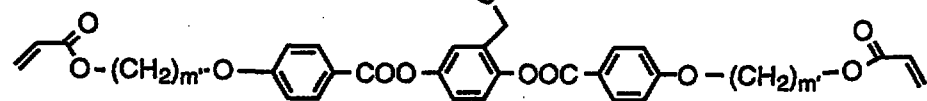
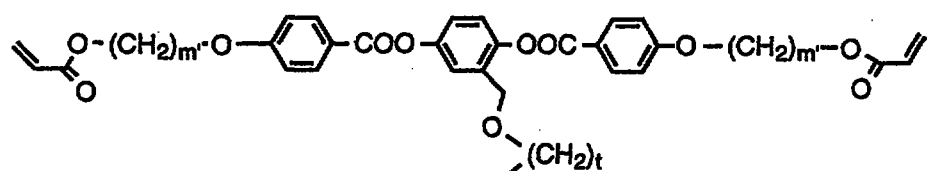


IV

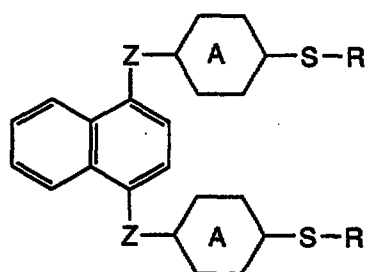


V

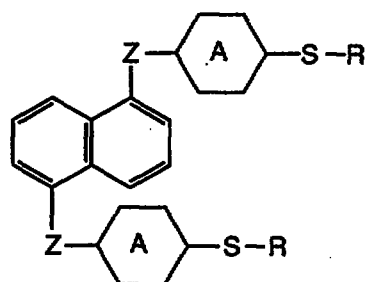
15



5



and



wherein

	X	signifies hydrogen, fluorine, chlorine, bromine or methyl;
	m'	signifies a whole number of 3 to 12;
5	t	signifies a whole number of 2 to 12;
	Z	signifies -OCH ₂ - or -OOC-;
	A	signifies 1,4-phenylene or 2- or 3-fluoro-1,4-phenylene;
	S	signifies -(CH ₂) _{m'} - or -(CH ₂) _{m'} O-; and
10	R	signifies CH ₂ =CH-COO-, CH ₂ =C(CH ₃)-COO-, CH ₂ =CH-O- or $\begin{array}{c} \text{H}_2\text{C}-\text{CH}- \\ \quad \quad \quad \text{O} \end{array}$.

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.

Example 1

0.43 g of N,N'-dicyclohexylcarbodiimide was added within 5 minutes while stirring to a solution of 0.1 g of trans-2,3-dihydroxy-1,4-dioxane, 0.9 g of 4-(4-[8-acryloyloxyoctyloxy]-phenylcarbonyloxy)benzoic acid and 0.05 g of 4-(dimethylamino)-pyridine in 25 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 chromatography gave 0.15 g of trans-2,3-bis[4-(4-[8-acryloyloxyoctyloxy]-phenylcarbonyloxy)phenylcarbonyloxy]-1,4-dioxane; m.p. (C-N) 98°C and cl.p. (N-I) 153°C.

The following compounds can be prepared in an analogous manner:

trans-2,3-Bis[4-(4-[3-acryloyloxypropyloxy]phenylcarbonyloxy)phenylcarbonyloxy]-1,4-dioxane;

- trans-2,3-bis[4-(4-[4-acryloyloxybutoxy]phenyl-carbonyloxy)phenylcarbonyloxy]-1,4-dioxane;
- trans-2,3-bis[4-(4-[5-acryloyloxypropyloxy]phenyl-carbonyloxy)phenylcarbonyloxy]-1,4-dioxane;
- 5 trans-2,3-bis[4-(4-[6-acryloyloxyhexyloxy]phenyl-carbonyloxy)phenylcarbonyloxy]-1,4-dioxane;
- trans-2,3-bis[4-(4-[7-acryloyloxyheptyloxy]phenyl-carbonyloxy)phenylcarbonyloxy]-1,4-dioxane;
- trans-2,3-bis[4-(4-[9-acryloyloxy-nonyloxy]phenyl-
- 10 carbonyloxy)phenylcarbonyloxy]-1,4-dioxane;
- trans-2,3-bis[4-(4-[10-acryloyloxydecyloxy]phenyl-carbonyloxy)phenylcarbonyloxy]-1,4-dioxane;
- trans-2,3-bis[4-(4-[11-acryloyloxyundecyloxy]phenyl-carbonyloxy)phenylcarbonyloxy]-1,4-dioxane;
- 15 trans-2,3-bis[4-(4-[12-acryloyloxydodecyloxy]phenyl-carbonyloxy)phenylcarbonyloxy]-1,4-dioxane;
- trans-2,3-bis(4-[3-acryloyloxypropyloxy]biphenyl-4'-carbonyloxy)-1,4-dioxane;
- trans-2,3-bis(4-[4-acryloyloxybutoxy]biphenyl-4'-
- 20 carbonyloxy)-1,4-dioxane;
- trans-2,3-bis(4-[5-acryloyloxypropyloxy]biphenyl-4'-carbonyloxy)-1,4-dioxane;
- trans-2,3-bis(4-[6-acryloyloxyhexyloxy]biphenyl-4'-carbonyloxy)-1,4-dioxane;
- 25 trans-2,3-bis(4-[7-acryloyloxyheptyloxy]biphenyl-4'-carbonyloxy)-1,4-dioxane;
- trans-2,3-bis(4-[8-acryloyloxyoctyloxy]biphenyl-4'-carbonyloxy)-1,4-dioxane;
- trans-2,3-bis(4-[9-acryloyloxy-nonyloxy]biphenyl-4'-
- 30 carbonyloxy)-1,4-dioxane;
- trans-2,3-bis(4-[10-acryloyloxydecyloxy]biphenyl-4'-carbonyloxy)-1,4-dioxane;
- trans-2,3-bis(4-[11-acryloyloxyundecyloxy]biphenyl-4'-carbonyloxy)-1,4-dioxane;
- 35 trans-2,3-bis(4-[12-acryloyloxydodecyloxy]biphenyl-4'-carbonyloxy)-1,4-dioxane;
- trans-2,3-bis[4-(5-[3-acryloyloxypropyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[4-acryloyloxybutyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[5-acryloyloxypropyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

5 trans-2,3-bis[4-(5-[6-acryloyloxyhexyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[7-acryloyloxyheptyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

10 trans-2,3-bis[4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[9-acryloyloxynonyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[10-acryloyloxydecyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

15 trans-2,3-bis[4-(5-[11-acryloyloxyundecyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

20 trans-2,3-bis[4-(5-[3-acryloyloxypropyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[4-acryloyloxybutyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[5-acryloyloxypropyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

25 trans-2,3-bis[4-(5-[6-acryloyloxyhexyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[7-acryloyloxyheptyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

30 trans-2,3-bis[4-(5-[8-acryloyloxyoctyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[9-acryloyloxynonyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[10-acryloyloxydecyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

35 trans-2,3-bis[4-(5-[11-acryloyloxyundecyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[12-acryloyloxydodecyloxy]pyridin-2-yl)phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[2-(4-[8-acryloyloxyoctyloxy]phenyl)-
pyrimidin-5-ylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[2-(4-[8-acryloyloxyoctyloxy]phenyl)pyridin-
5-ylcarbonyloxy]-1,4-dioxane;

5 trans-2,3-bis[trans-4-(trans-4-[3-acryloyloxypropyl]-
cyclohexyl)cyclohexancarbonyloxy]-1,4-dioxane;

trans-2,3-bis[trans-4-(2-[trans-4-(3-acryloyloxypropyl)-
cyclohexyl]ethyl)cyclohexancarbonyloxy]-1,4-dioxane;

10 trans-2,3-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-
phenylcarbonyloxy]-1,4-dioxane;

trans-2,3-bis[4-(2-[trans-4-(3-acryloyloxypropyl)cyclohexyl]-
ethyl)phenylcarbonyloxy]-1,4-dioxane.

Example 2

15

A solution of 0.2 g of trans-2,3-dihydroxy-1,4-dioxane,
0.5 g of sodium hydride and 50 ml of tetrahydrofuran is stirred
for 7 hours. 1.1 g of 4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-
yl)benzyl tosylate are added and the mixture is stirred at room
20 temperature overnight, poured into 100 ml of water and then
extracted three times with 50 ml of diethyl ether each 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
25 residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2) and
two-fold recrystallization from a cyclohexane/ethyl acetate
mixture (vol. 8:2) of the fractions which are pure according to
thin-layer chromatography gives 1.1 g of trans-2,3-bis[4-(5-[8-
acryloyloxyoctyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane.

30

The following compounds can be prepared in an analogous
manner:

trans-2,3-Bis[4-(4-[3-acryloyloxypropyloxy]phenyl)-
35 carbonyloxy]benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(4-[4-acryloyloxybutoxy]phenyl)-
carbonyloxy]benzyloxy]-1,4-dioxane;

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

trans-2,3-bis[4-(5-[5-acryloyloxypropyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[6-acryloyloxyhexyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane;

5 trans-2,3-bis[4-(5-[7-acryloyloxyheptyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane;

10 trans-2,3-bis[4-(5-[9-acryloyloxynonyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[10-acryloyloxydecyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[11-acryloyloxyundecyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane;

15 trans-2,3-bis[4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[3-acryloyloxypropyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

20 trans-2,3-bis[4-(5-[4-acryloyloxybutyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[5-acryloyloxypropyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[6-acryloyloxyhexyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

25 trans-2,3-bis[4-(5-[7-acryloyloxyheptyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[8-acryloyloxyoctyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

30 trans-2,3-bis[4-(5-[9-acryloyloxynonyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[10-acryloyloxydecyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[11-acryloyloxyundecyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

35 trans-2,3-bis[4-(5-[12-acryloyloxydodecyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[4-(5-[8-acryloyloxyoctyloxy]pyridin-2-yl)benzyloxy]-1,4-dioxane;

trans-2,3-bis[(2-[4-(8-acryloyloxyoctyloxy)phenyl]-
pyrimidin-5-yl)methoxy]-1,4-dioxane;

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

5 trans-2,3-bis[(trans-4-[2-(trans-4-[3-acryloyloxypropyl]-
cyclohexyl)ethyl]cyclohexyl)methoxy]-1,4-dioxane;

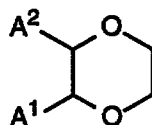
trans-2,3-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-
benzyloxy]-1,4-dioxane;

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



Claims

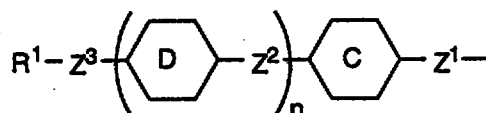
1. Compounds of the general formula



wherein

A¹ and A² each represent a cross-linkable, mesogenic residue.

2. Compounds according to claim 1, wherein the mesogenic residues A¹ and A² signify residues 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-(CH₂)_m-, -(CH₂)_mO-, -O(CH₂)_m-, -COO-, -OOC-, -(CH₂)_mCOO- or -(CH₂)_mOOC-;

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

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



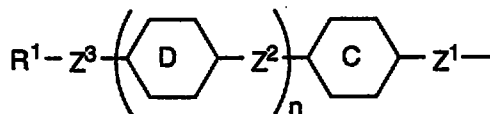
signifies hydrogen or fluorine;
signifies 0, 1 or 2;
signifies a whole number of 1 to 16; and
signifies a cross-linkable group of the
structure $\text{CH}_2=\text{CH}-$, $\text{CH}_2=\text{CH}-\text{COO}-$,
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-$, $\text{CH}_2=\text{C}(\text{Cl})-\text{COO}-$,
 $\text{CH}_2=\text{C}(\text{Ph})-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{COO}-\text{Ph}-$,
 $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-$,
 $\text{CH}_2=\text{C}(\text{Cl})-\text{CONH}-$, $\text{CH}_2=\text{C}(\text{Ph})-\text{CONH}-$,
 $\text{CH}_2=\text{C}(\text{COOR}')-\text{CH}_2-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{O}-$,
 $\text{CH}_2=\text{CH}-\text{OOC}-$, $\text{Ph}-\text{CH}=\text{CH}-$, $\text{CH}_3-\text{C}(=\text{NR}')-$,
cis,trans $\text{HOO}-\text{CR}'=\text{CR}'-\text{COO}-$,

$$\begin{array}{c} \text{H}_2\text{C}-\text{CH}- \\ \quad \diagup \quad \diagdown \\ \quad \text{O} \end{array}, \quad \begin{array}{c} \text{R}' \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{CH}=\text{CH}- \end{array} \quad \text{or} \quad \begin{array}{c} \text{R}'' \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{CH}=\text{CH}-\text{COO}- \end{array};$$

Ph signifies phenyl;
R' signifies lower alkyl; and
R'' signifies methyl, methoxy, cyano or halogen;

20 with the proviso that R^1-Z^3 contains no -O-O- or -N-O- groups.

3. Compounds according to claim 1 or 2, wherein the mesogenic residues A¹ and A² signify residues 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; signifies $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{COO}-$, $-\text{OOC}-$, $-(\text{CH}_2)_4-$ or $-(\text{CH}_2)_3\text{O}-$;

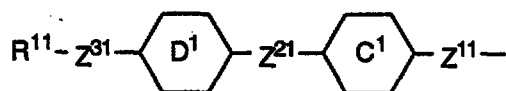


	Z ²	signifies a single bond, -CH ₂ CH ₂ -, -CH ₂ O-, -OCH ₂ -, -COO-, -OOC-, -(CH ₂) ₄ -, -O(CH ₂) ₃ - or -(CH ₂) ₃ O-;
5	Z ³	signifies -(CY ₂) _m -, -O(CY ₂) _m -, -(CY ₂) _m O-, -(CY ₂) _m COO-, -(CY ₂) _m OOC-, -[Si[(CH ₃) ₂]O] _m -, -OCH ₂ [Si[(CH ₃) ₂]O] _m Si[(CH ₃) ₂]CH ₂ O- or -NHCH ₂ [Si[(CH 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
	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')-, cis,trans HOO-CR'=CR'-COO-,
15		
20		
		$\text{H}_2\text{C}-\text{CH}-$ O , R'-C₆H₄-CH=CH- or R''-C₆H₄-CH=CH-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 claim 4, wherein the residues A¹ and A² signify a residue of formula II-a



II-a

wherein

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

Z¹¹ signifies -CH₂CH₂-, -CH₂O-, -COO- or -OOC-;

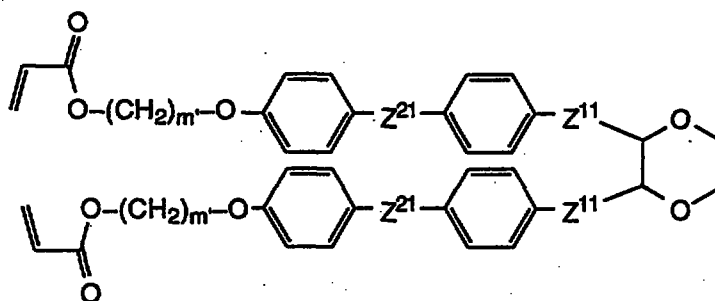
Z²¹ signifies a single bond, -CH₂O-, -COO-, -OOC-;

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 $\text{H}_2\text{C}-\text{CH}-\text{O}$.

6. Compounds in accordance with claim 5 of the formula



I-A

wherein

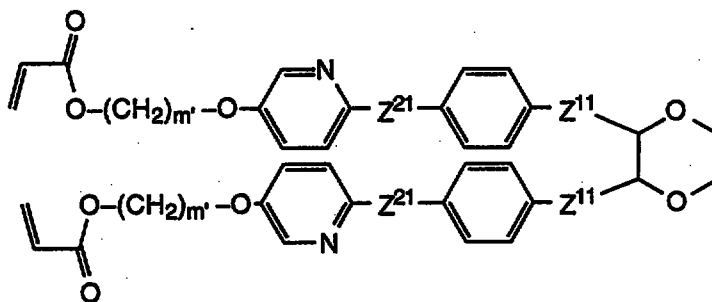
Z¹¹ signifies -COO-;

Z²¹ signifies a single bond or -COO-, especially -COO-; and

m' signifies a whole number of 3 to 12.



7. Compounds according to claim 5 of the formula



I - B

5 wherein

Z¹¹

signifies -COO-;

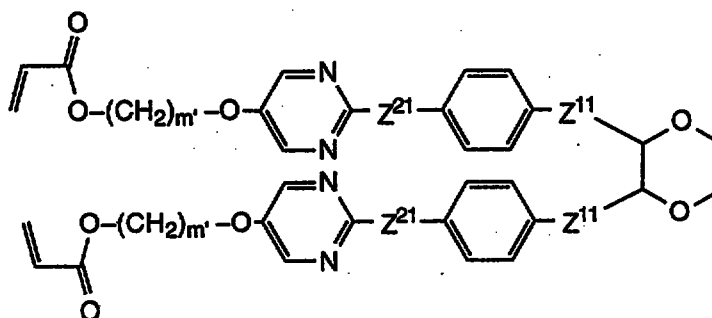
Z²¹signifies a single bond or -COO-,
especially -COO-; and

m'

signifies a whole number of 3 to 12.

10

8. Compounds according to claim 5 of the formula



I - C

15 wherein

Z¹¹

signifies -COO-;

Z²¹signifies a single bond or -COO-,
especially -COO-; and

m'

signifies a whole number of 3 to 12.

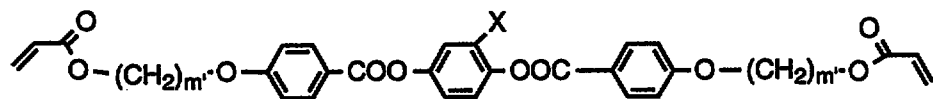
20

9. Compounds according to any one of claims 6 to 8,
wherein Z¹¹ and Z²¹ signify -COO-.

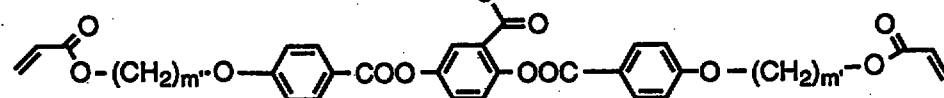
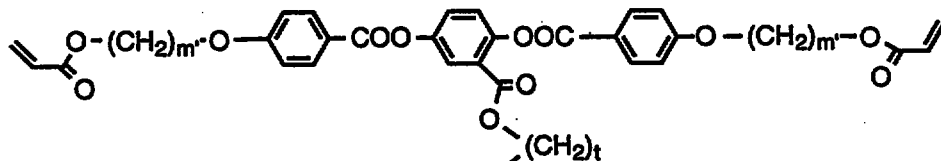
10. A cross-linkable, liquid crystalline mixture
25 consisting of at least 2 components, wherein at least one
component is a compound of formula I defined in claim 1.



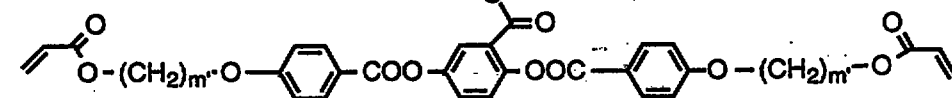
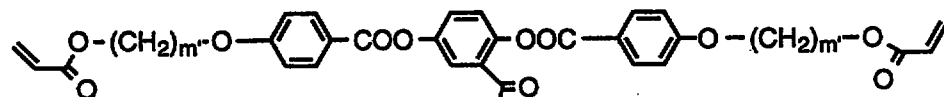
11. A cross-linkable, liquid crystalline mixture according to claim 10, which contains, in addition to one or more compounds of formula I, one or more compounds from the group of the 5 formulae



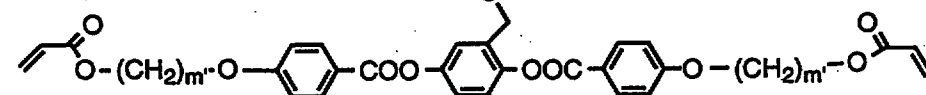
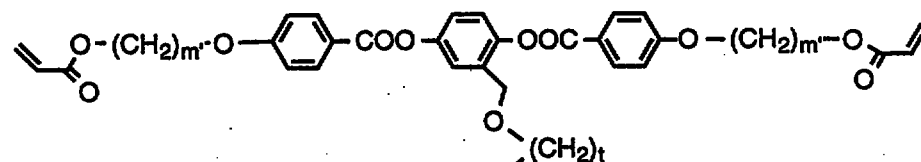
III



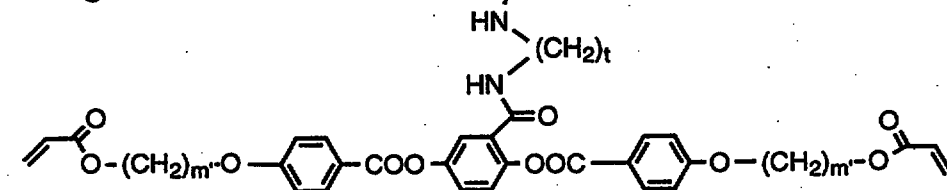
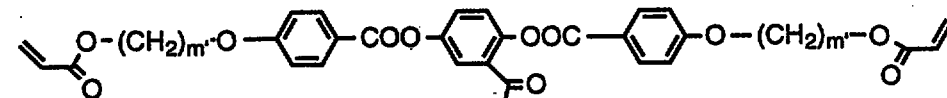
IV



V



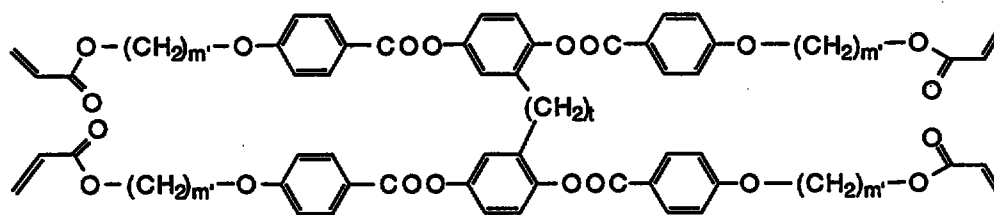
VI



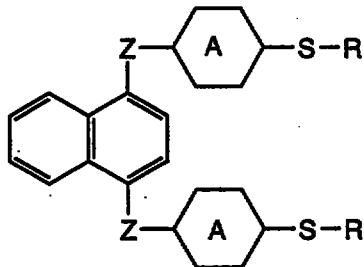
VII



29

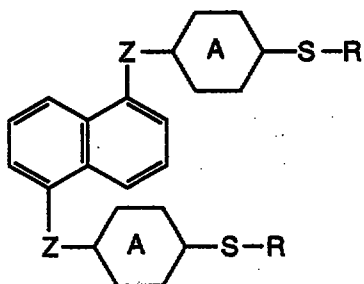


VIII



IX

and



X

5

wherein

X

signifies hydrogen, fluorine, chlorine, bromine or methyl;

m'

signifies a whole number of 3 to 12;

10

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;

S

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

15

R

signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-,
CH₂=CH-O- or $\begin{matrix} \text{H}_2\text{C} & \text{CH} \\ & \diagdown \quad \diagup \\ & \text{O} \end{matrix}$

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

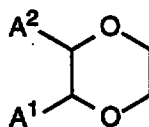
20



13. The use of cross-linkable liquid crystalline mixtures according to claim 10 or 11 in their cross-linked state for optical components.

Abstract

5 The present invention is concerned with photo cross-linkable liquid crystalline compounds of the general formula



10 wherein
 A¹ and A² each represent a cross-linkable, meso-
 genic residue,
liquid crystalline mixtures which contain such compounds and
their use in the cross-linked state as optical components.

15

This Sheet Has Been Replaced



1-888-0100

31 JAN 1997

PHOTO-CROSS-LINKABLE LIQUID CRYSTALLINE 1,4-DIOXAN-2,3-DIYL-
DERIVATIVES

5 The present invention is concerned with photo cross-linkable liquid crystalline 1,4-dioxane-2,3-diyl derivatives, liquid crystalline mixtures which contain such compounds and their use in the cross-linked state for optical components.

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

20 Further properties such as, for example, the birefringence, the refractive index, the transparency, etc. must fulfil different requirements depending on the field of use. Thus, materials for optical filters should have a strong absorption in a direction perpendicular to the filter surface.

25

In addition to the general use of photo cross-linkable liquid crystals for optical components, such liquid crystalline materials are suitable as a cladding for glass fibres for optical data transmission. The use of such materials increases the elastic
30 modulus in the longitudinal axis of the fibre, reduces the thermal expansion coefficient and avoids microdistortion losses. This leads to an increased mechanical stability.

35 The photo cross-linkable liquid crystals must have a good chemical and thermal stability, good solubility in common solvents and a good stability towards electric fields and electromagnetic radiation. They should have a suitable mesophase in a temperature range of about 25°C to about +100°C, especially of about 25°C to about +80°C. Moreover, it is important that the

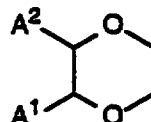
31 JAN 1997

31

PHOTO-CROSS-LINKABLE LIQUID CRYSTALLINE 1,4-DIOXAN-2,3-DIYL-
DERIVATIVES

Abstract

5 The present invention is concerned with photo cross-linkable liquid crystalline compounds of the general formula



10 wherein
 A¹ and A² each represent a cross-linkable, meso-
 genic residue,
liquid crystalline mixtures which contain such compounds and
their use in the cross-linked state as optical components.

15