

## Optically active smectic photo-cross-linkable Liquid Crystals

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

Photo-cross linkable liquid crystals provided with an appropriate amount of a photoinitiator can be orientated on a substrate or in a cell by suitable orientating 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 preserved even at high temperatures. Such layers can be, for example, parts of hybrid layers as are described in Swiss Patent Applications CH 2016/94 and CH 2017/94. Thus, optical components, such as, for example, wave guides, optical screens and filters, components having piezoelectric properties and those having non-linear optical (NLO) properties, etc., can be produced. Such optical components are used, for example, in frequency doubling (SHG).

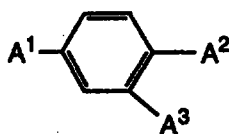
Further properties such as, for example, the birefringence, the refractive index, transparency, etc. must fulfil different requirements depending on the field of use. For example, materials for frequency doubling (SHG) should have a strong coupling between the direction of maximum hyperpolarizability and the polar axis in order that the degree of efficiency of the signal doubling is high.

Moreover, the photo-cross linkable liquid crystals must have a good chemical and thermal stability, good solubility in usual solvents and a good stability towards electric fields and electromagnetic radiation. Furthermore, they should have a suitable mesophase from about 25°C to about 100°C, especially from about 25°C to about 80°C, for example they should have a broad chiral smectic mesophase for the applications referred to above.

Since liquid crystals are usually used as mixtures of several components, it is important that the components have a good miscibility with one another. Components which in mixtures bring about a frequency doubling or lead to optical activity are usually not liquid crystalline themselves. They therefore usually have the disadvantage that they lead to a large decrease of the phase transition temperatures and accordingly can be used only in low concentrations. This leads to a small SHG degree of efficiency. Mixtures consisting of photo-cross linkable liquid crystals and non-photo-cross linkable liquid crystals and/or optically active (chiral) additives permit a relaxation of the non-cross linkable components and thereby lead to a diminishing of the SHG signal. On the other hand, networks in which the active components are incorporated permit high concentrations of these active additives. At the same time, the orientating relaxation is prevented by the fixation in the network. Blue or green light can be produced by using in such networks colouring substances which absorb at the wavelength of the SHG light generated by a laser diode. Such networks have the disadvantage that usually they do not have sufficient long-term stability.

There is accordingly the need to produce photo-cross linkable contents which satisfy the aforementioned requirements, can be structured, have an excellent thermal stability and long-term stability and a high SHG degree of efficiency.

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



I

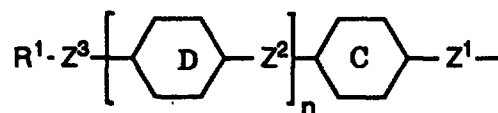
wherein  
 A¹, A² each independently signify a cross-linkable mesogenic residue and

A<sup>3</sup> signifies an optically active, mesogenic residue.

The mesogenic cross-linkable residues A<sup>1</sup> and A<sup>2</sup> can be different or the same. Mesogenic residues will be known to a person skilled in the art and are described, for example, in Flüssigkristalle in Tabellen, Deutscher Verlag für Grundstoffindustrie Leipzig, 1984, volume II. In order for the known mesogenic residues to be suitable for the above purpose, they are provided terminally with a polymerizable residue.

Since the compounds in accordance with the invention or their mixtures have a tilted smectic phase, they can be directed by the application of an electric field prior to the cross-linking. The pitch is thereby unwound and a uniform, ferroelectric layer is produced.

Preferred compounds of formula I are those in which the cross-linkable, mesogenic residues A<sup>1</sup> and A<sup>2</sup> are the same and signify residues of the formula



II

wherein

rings C and D

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

Z<sup>1</sup>

signifies a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-, -COO-, -OOC-, -(CH<sub>2</sub>)<sub>4</sub>- or -(CH<sub>2</sub>)<sub>3</sub>O-;

Z<sup>2</sup>

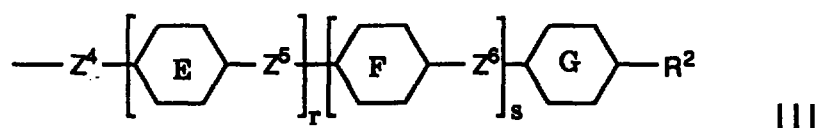
signifies a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -COO-, -OOC-, -(CH<sub>2</sub>)<sub>4</sub>-, -O(CH<sub>2</sub>)<sub>3</sub>- or -(CH<sub>2</sub>)<sub>3</sub>O-;

Z<sup>3</sup>

signifies -(CH<sub>2</sub>)<sub>m</sub>-, -(CH<sub>2</sub>)<sub>m</sub>O-, -(CH<sub>2</sub>)<sub>m</sub>COO- or -(CH<sub>2</sub>)<sub>m</sub>OOC-;

n signifies 0 or 1;  
 m signifies a whole number of 1 to 16; and  
 R<sup>1</sup> signifies a cross-linkable group such as  
 acrylate, methacrylate, 2-chloroacrylate,  
 2-phenylacrylate, acryloylphenylene,  
 acrylamide, methacrylamide, 2-phenyl-  
 acrylamide, epoxy, itaconic acid ester,  
 vinyl ether, vinyl ester, styrene deriv-  
 ative, maleic acid derivative or fumaric  
 acid derivative or a cinnamic acid  
 derivative, which is optionally substituted  
 with methyl, methoxy, cyano and/or  
 halogen.

In the compounds of formula I the optically active,  
 mesogenic residue A<sup>3</sup> preferably signifies a residue of the  
 general formula



wherein  
 rings E and F

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

ring G

signifies 1,4-phenylene, which is unsub-  
 stituted or mono- or disubstituted with  
 halogen, methyl, dimethylamino, amino,  
 nitro and/or cyano;

Z<sup>4</sup>

signifies a single bond, -(CH<sub>2</sub>)<sub>p</sub>-,  
 -(CH<sub>2</sub>)<sub>p</sub>O-, -O(CH<sub>2</sub>)<sub>p</sub>-, -(CH<sub>2</sub>)<sub>p</sub>COO-,  
 -OOC(CH<sub>2</sub>)<sub>p</sub>-, -(CH<sub>2</sub>)<sub>p</sub>OOC-, -COO(CH<sub>2</sub>)<sub>p</sub>-,  
 -OOC(CH<sub>2</sub>)<sub>p</sub>OOC-, -O(CH<sub>2</sub>)<sub>p</sub>OOC- or  
 -COO(CH<sub>2</sub>)<sub>p</sub>O- ;

Z<sup>5</sup>, Z<sup>6</sup>

signify a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-,

-OCH<sub>2</sub>-, -COO-, -OOC-, -(CH<sub>2</sub>)<sub>4</sub>-, -O(CH<sub>2</sub>)<sub>3</sub>-  
or -(CH<sub>2</sub>)<sub>3</sub>O-;

p

signifies a whole number of 1 to 16;

r, s

signify 0 or 1; and

5

R<sup>2</sup>

signifies an optically active group such as  
(S)- or (R)-2-butyloxy, (S)- or (R)-2-  
pentyloxy, (S)- or (R)-2-hexyloxy, (S)- or  
(R)-2-heptyloxy, (S)- or (R)-2-octyloxy or  
alkyl, alkoxy or alkanoyloxy with 4 to 8  
10 carbon atoms, which is substituted with  
methyl, methoxy, cyano and/or halogen.

10

The term "1,4-phenylene, which is optionally substituted  
with halogen, methyl and/or cyano," signifies in the scope of the  
15 present invention 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-  
fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene, 2-chloro-1,4-  
phenylene, 3-chloro-1,4-phenylene, 2,3-dichloro-1,4-phenylene,  
2-cyano-1,4-phenylene, 3-cyano-1,4-phenylene, 2,3-dicyano-1,4-  
phenylene, 2-methyl-1,4-phenylene, 3-methyl-1,4-phenylene and  
20 the like.

20

The term "1,4-phenylene, which is unsubstituted or mono-  
or disubstituted with halogen, methyl, dimethylamino, amino,  
nitro and/or cyano," signifies in the scope of the present  
25 invention 1,4-phenylene or, for example, 2-amino-5-nitro-1,4-  
phenylene, 5-amino-2-nitro-1,4-phenylene, 2-dimethylamino-5-  
nitro-1,4-phenylene or 5-dimethylamino-2-nitro-1,4-phenylene  
and the like.

25

30 Halogen stands for fluorine, chlorine, bromine and iodine,  
especially for fluorine or chlorine.

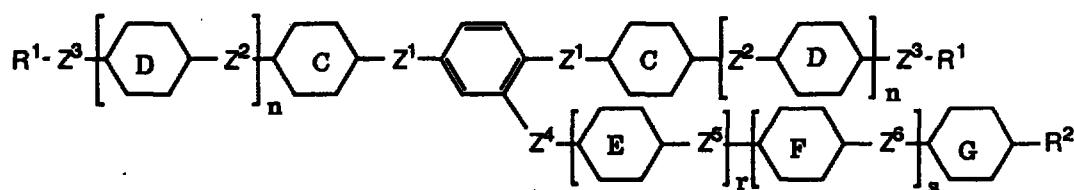
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The term "alkyl, alkoxy or alkanoyloxy with 4 to 8 carbon  
atoms, which is substituted with methyl, methoxy, cyano and/or  
35 halogen," signifies in the scope of the present invention optically  
active alkyl, alkoxy or alkanoyloxy groups such as, for example,  
(S)- or (R)-2-methylbutyl, (S)- or (R)-2-methylpentyl, (S)- or  
(R)-2-methylhexyl, (S)- or (R)-2-methylheptyl, (S)- or (R)-2-

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methoxybutyl, (S)- or (R)-2-methoxypentyl, (S)- or (R)-2-methoxyhexyl, (S)- or (R)-2-methoxyheptyl, (S)- or (R)-1-cyanobutyl, (S)- or (R)-1-cyanopentyl, (S)- or (R)-1-cyanoheptyl, (S)- or (R)-2-cyanobutyl, (S)- or (R)-2-cyanopentyl, (S)- or (R)-2-cyanoheptyl, (S)- or (R)-1-fluorobutyl, (S)- or (R)-1-fluoropentyl, (S)- or (R)-1-fluoroheptyl, (S)- or (R)-2-fluorobutyl, (S)- or (R)-2-fluoropentyl, (S)- or (R)-2-fluoroheptyl, (S)- or (R)-1-chlorobutyl, (S)- or (R)-1-chloropentyl, (S)- or (R)-1-chloroheptyl, (S)- or (R)-2-chlorobutyl, (S)- or (R)-2-chloropentyl, (S)- or (R)-2-chloroheptyl or (S)- or (R)-2-chloroheptyl and the like.

Preferred compounds of formula I are therefore the compounds of the general formula



I-1

wherein the symbols have the aforementioned significance.

The mesophase type of the compounds of formula I-1 in accordance with the invention can be influenced by varying rings C, D, E and F. Thus, aromatic rings are more inclined to produce smectic phases. Preferably, rings C and D each independently signify 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, pyridine-2,5-diyl or pyrimidine-2,5-diyl, especially 1,4-phenylene, 2-fluoro-1,4-phenylene or 3-fluoro-1,4-phenylene.

Rings E and F in the compounds in accordance with the invention preferably signify 1,4-phenylene, while ring G preferably signifies 2-amino-5-nitro-1,4-phenylene or 5-amino-2-nitro-1,4-phenylene.

Especially preferred compounds of formula I-1 are compounds in which Z<sup>1</sup> signifies -CH<sub>2</sub>O-, -COO- or -OOC-; and Z<sup>2</sup> signifies a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -COO- or -OOC-.

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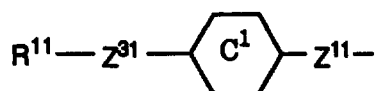
In especially preferred compounds of formula I-1 the residue R<sup>1</sup> signifies acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-phenylacrylamide, epoxy, vinyl ether, vinyl ester, styrene derivative, maleic acid derivative or fumaric acid derivative and the like. These are thus residues which can be cross-linked photochemically after orientation of the compounds of formula I in a field.

15 Acrylate, methacrylate, vinyloxy and epoxy are especially preferred residues R<sup>1</sup>.

(S)- or (R)-2-Butyloxy, (S)- or (R)-2-pentyloxy, (S)- or (R)-2-hexyloxy, (S)- or (R)-2-heptyloxy and (S)- or (R)-2-octyloxy are preferably used as optically active residues R<sup>2</sup>.

20

Preferably, the mesogenic residues A<sup>1</sup> and A<sup>2</sup> are the same and signify a residue of formula II in which n = 0 such as, for example



25

II-a

wherein

R<sup>11</sup> signifies acrylate, methacrylate or epoxy;

Z<sup>31</sup> signifies -(CH<sub>2</sub>)<sub>t</sub>-, -(CH<sub>2</sub>)<sub>t</sub>O-, -(CH<sub>2</sub>)<sub>t</sub>COO- or -(CH<sub>2</sub>)<sub>t</sub>OOC-;

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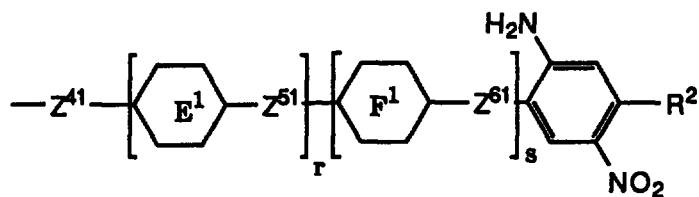
t signifies a whole number from 4 to 12;

ring C<sup>1</sup> signifies 1,4-phenylene, 2-fluoro-1,4-phenylene or 3-fluoro-1,4-phenylene; and

Z<sup>11</sup> signifies -CH<sub>2</sub>O-, -COO- or -OOC-.

35

Preferably, the mesogenic residue A<sup>3</sup> signifies a residue of formula III such as, for example



III-a

wherein

R<sup>2</sup> signifies (S)- or (R)-2-butyloxy, (S)- or (R)-2-pentyloxy, (S)- or (R)-2-hexyloxy, (S)- or (R)-2-heptyloxy or (S)- or (R)-2-octyloxy;

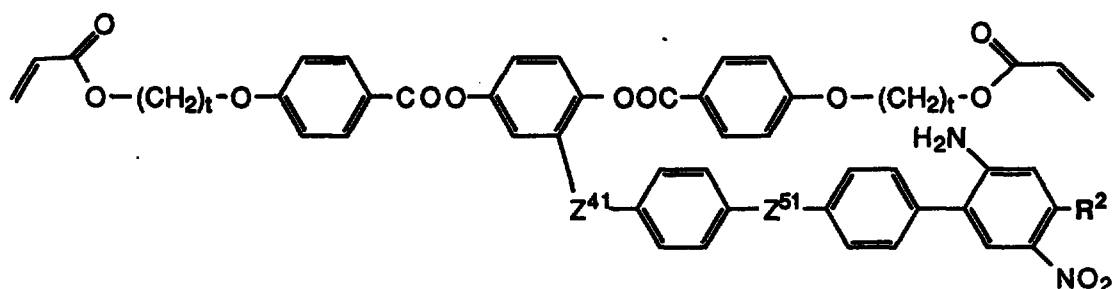
r, s signify 0 or 1;

Z<sup>41</sup> signifies -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, -OCH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>O-, -COOCH<sub>2</sub>- or -CH<sub>2</sub>OOC-;

Z<sup>51</sup>, Z<sup>61</sup> signify a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-, -COO-, -OOC, -(CH<sub>2</sub>)<sub>4</sub>- or -(CH<sub>2</sub>)<sub>3</sub>O-; and

rings E<sup>1</sup> and F<sup>1</sup> signify 1,4-phenylene.

Quite particularly preferred compounds of formula I-1 are therefore the compounds of the formula



I-2

wherein

t is a whole number from 4 to 12;

R<sup>2</sup> signifies (S)- or (R)-2-butyloxy, (S)- or (R)-2-pentyloxy, (S)- or (R)-2-hexyloxy, (S)- or (R)-2-heptyloxy or (S)- or (R)-2-octyloxy;

Z<sup>41</sup> signifies -COOCH<sub>2</sub>-; and

Z<sup>51</sup> signifies a single bond, -COO- or -OOC-.

The compounds of general formula I in accordance with the invention are very readily accessible synthetically and can be produced in a manner known per se, for example analogously to  
5 the methods illustrated in Schemes 1 and 2 as well as in the Examples.

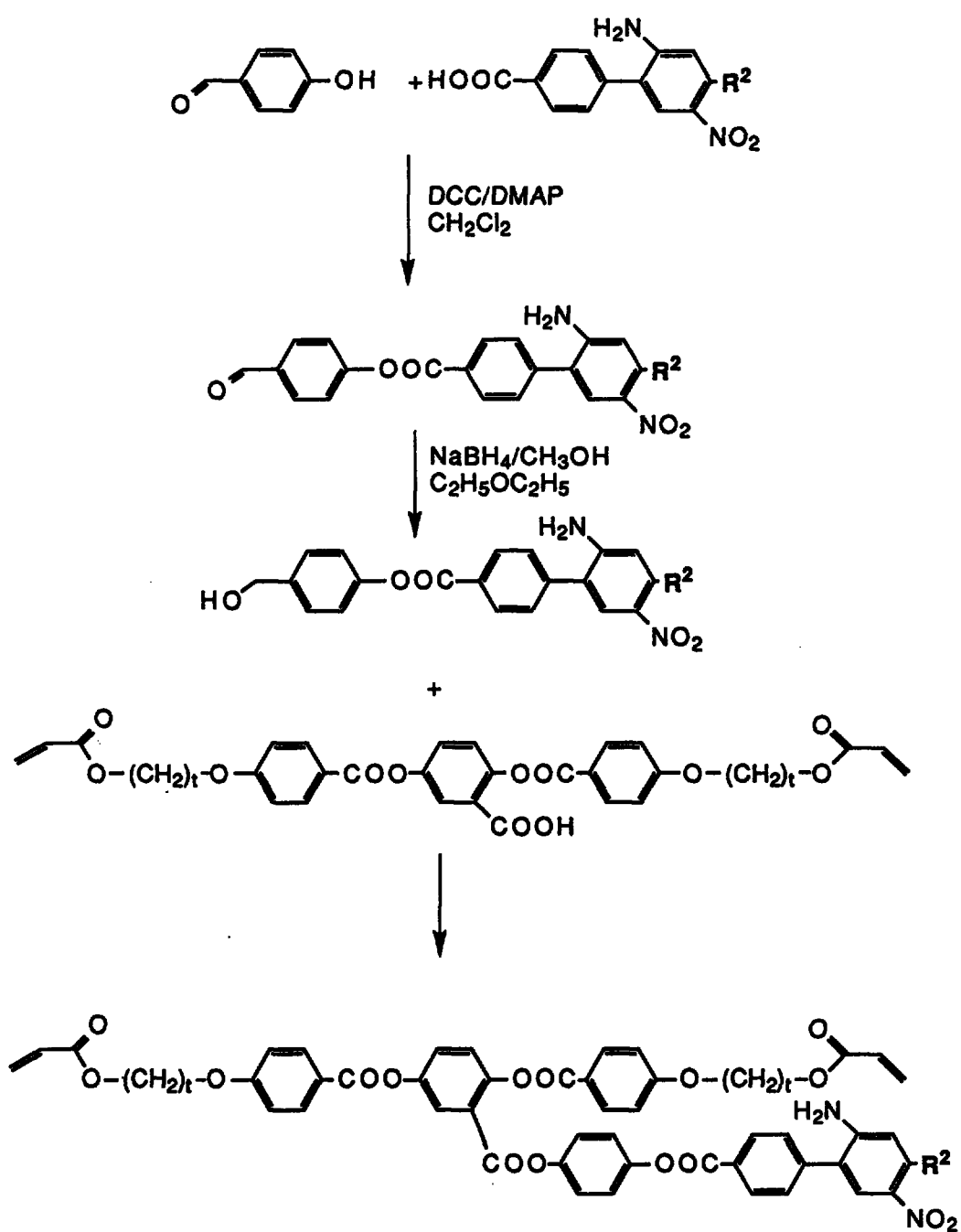
The mesogenic residues of formula II and III are known or are analogues of known structures and can be prepared in a  
10 manner known per se and subsequently linked with the aromatics.

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.

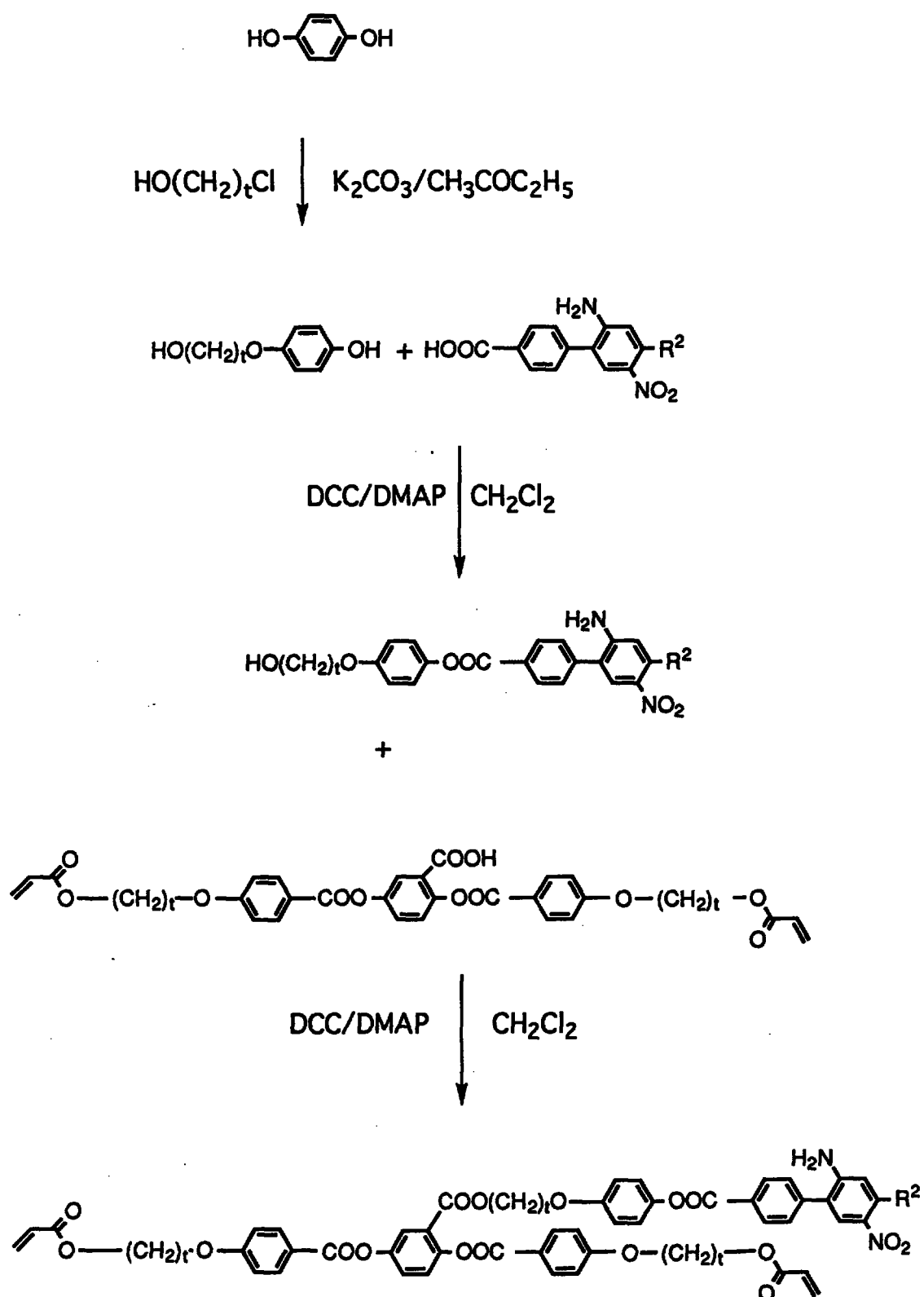
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In the Schemes the symbols have the significances given above.

Scheme 1



Scheme 2



The compounds of general formula I in accordance with the invention are readily accessible synthetically and can be produced, for example, in a manner known per se from optically active alcohols (derivatives of formula III) and bis[2,5-bis(4-[n-  
5 acryloyloxyalkyloxy)]phenylcarboxy)benzoic acids. The esterification can be effected, for example, in the presence of N,N'-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in dichloromethane or another suitable solvent such as e.g. chloroform.

10 Further, compounds of formula I can be produced by firstly etherifying 4-benzaldehyde with  $\omega$ -halo-1-alcohol derivatives, reducing the aldehyde with sodium borohydride to the benzyl alcohol derivative of formula II, etherifying this derivative with  
15 2,5-dihydroxybenzaldehyde in a Mitsunobu reaction, then esterifying with acrylic acid, oxidizing to the corresponding benzoic acid with Jones' reagent and subsequently esterifying with optically active alcohols (derivatives of formula III) as described above.

20 The optically active alcohols (derivatives of formula III) can be prepared, for example, from the esterification product of 4-hydroxybenzaldehyde with 4-[4-(2-amino-5-nitro-4-[(S)-2-alkyloxy]phenyl)-benzoic acids by reduction with sodium borohydride.  
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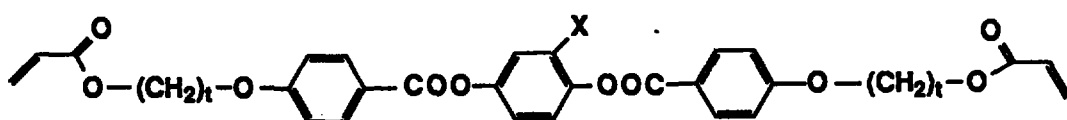
Asymmetric compounds, i.e. compounds in which residue A<sup>1</sup> and residue A<sup>2</sup> are different, can be produced by mono-esterifying  
30 2,5-dihydroxybenzaldehyde with a 4-(n-acryloyloxyalkyloxy)-benzoic acid to the monoester and then again esterifying with another 4-(n-acryloyloxyalkyloxy)benzoic acid to the diester. Oxidation of this diester with Jones' reagent gives the corresponding asymmetric [2,5-bis(4-[n-acryloyloxyalkyloxy)]phenyl-  
35 carboxy)benzoic acid which is subsequently reacted with an alcohol (derivative of formula III). The starting materials are known and are to some extent commercially available.

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

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

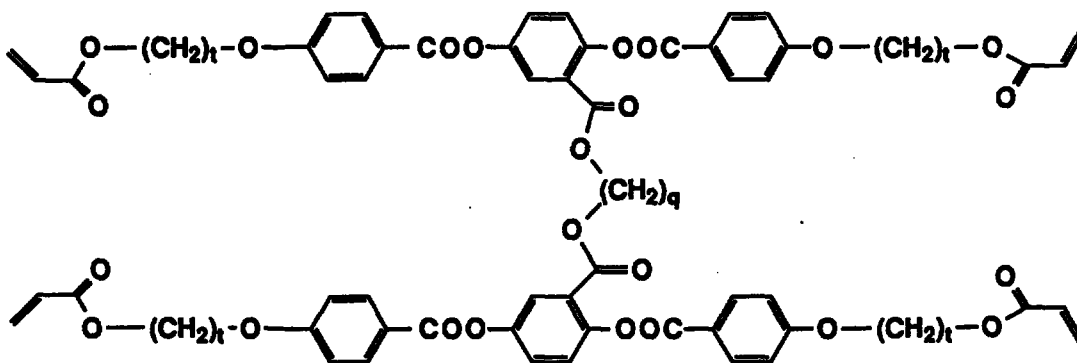
Having regard to the good solubility of the compounds of formula I and having regard to their good miscibility with one  
15 another, the content of different compounds of formula I in the mixtures in accordance with the invention can be high and can amount to 100 wt.%.

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

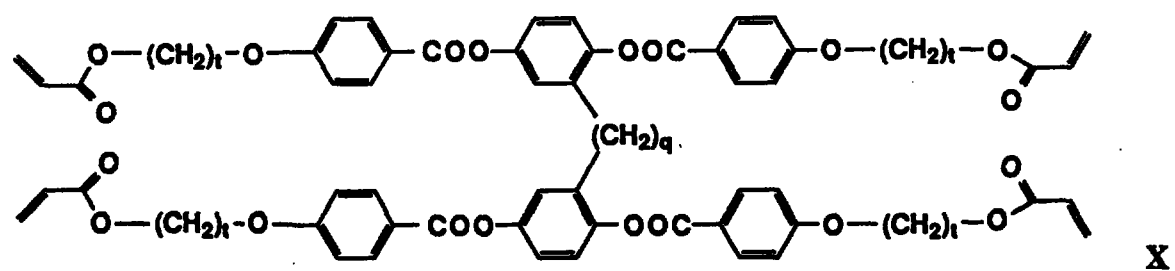
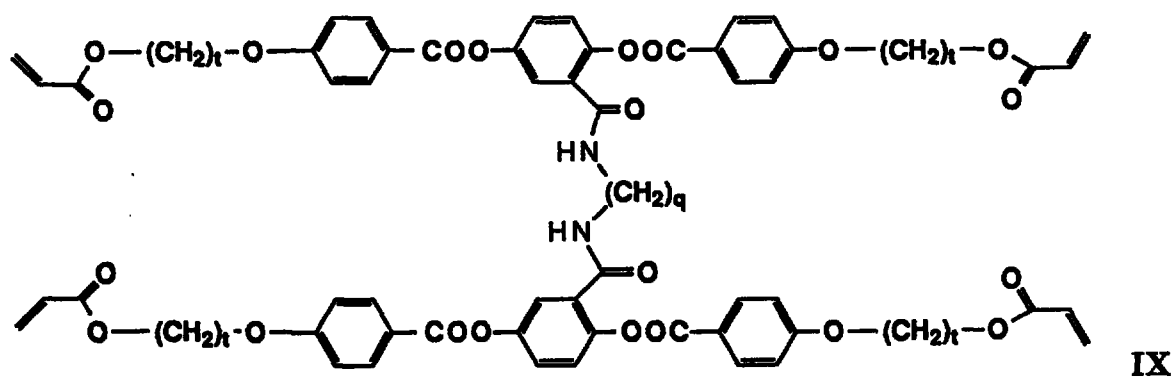
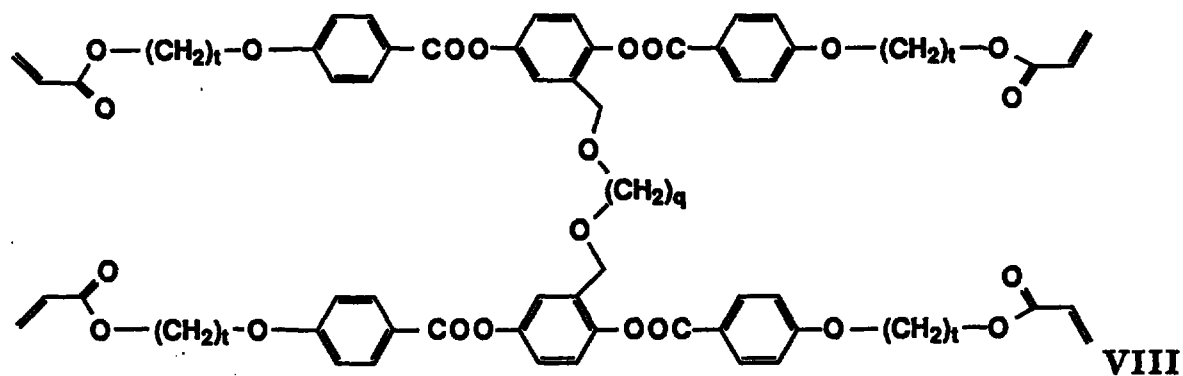
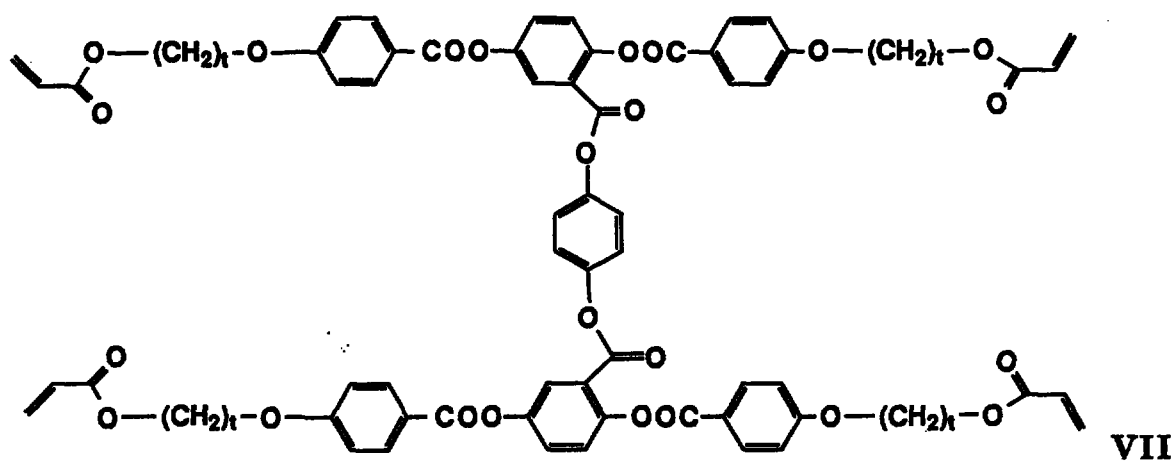


V

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VI



wherein t signifies a whole number from 4 to 12 and q signifies a whole number from 2 to 12.

5 The production of the compounds of formula I as well as liquid crystalline mixtures containing these compounds are illustrated in more detail by the following Examples. C signifies a crystalline phase, S signifies a smectic phase, N\* signifies the chiral nematic phase and I signifies the isotropic phase. "ac" signifies alternating current and "dc" signifies direct current. Optical antipodes have in each case "mirror image properties", i.e. the same melting point etc., but lead to opposite helical rotation and opposite circular polarization of the reflected light.

15

#### Example 1

0.2 g of N,N'-dicyclodicyclohexylcarbodiimide was added at room temperature while stirring to a solution of 0.6 g of 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarboxy)benzoic acid, 0.4 g of 4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]-phenyl)benzoyloxy]phenylmethanol and 0.04 g of 4-dimethylaminopyridine in 20 ml of dichloromethane. The reaction mixture was stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of dichloromethane each time. The organic phases were washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and subsequently concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl acetate (vol. 1:1) and two-fold recrystallization from acetone of the fractions which were pure according to thin-layer chromatography gave 0.4 g of (4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]-phenyl)-methyl 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarboxy)benzoate; m.p. (C-I) 100°C, Sc\*-N\*, 96°C, cl.p. (N\*-I) 100°C.

35

The (4-[4-(5-amino-2-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenyl)methanol used as the starting material was prepared as follows:

a) A mixture of 0.13 g of sodium borohydride and 15 ml of water was treated dropwise at 0°C with a solution of 0.8 g of 4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]-benzaldehyde in 100 ml of dioxan. The reaction mixture was stirred at 0°C for a further 60 minutes and then at room temperature for 10 minutes and thereafter poured into 100 ml of dichloromethane. The organic phase was separated and washed twice with 100 ml of water each time. The aqueous phases were extracted twice with 50 ml of dichloromethane each time. The combined organic phases were then washed twice with 100 ml of water each time, dried over magnesium sulphate, the suspension was filtered and the filtrate was concentrated. The residue was used in the next step without further purification.

b) 0.6 g of N,N'-dicyclodicyclohexylcarbodiimide was added at room temperature while stirring to a solution of 1.0 g of 4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoic acid, 0.3 g of 4-hydroxybenzaldehyde and 0.04 g of 4-dimethylaminopyridine in 20 ml of dichloromethane. The reaction mixture was stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of dichloromethane each time. The organic phases were washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate was subsequently concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl acetate (vol. 1:1) and two-fold recrystallization from ethanol of the fractions which were pure according to thin-layer chromatography gave 0.9 g of 4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]benzaldehyde; m.p. (C-I) 77-78°C.

The following compounds can be produced in an analogous manner:

(4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenyl)methyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenyl-carboxy)benzoate.

(4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenyl)methyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarboxy)benzoate.

5 (4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenyl)methyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarboxy)benzoate.

(4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenyl)methyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarboxy)benzoate.

10 (4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenyl)methyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate; m.p. (C-SA) 108°C; cl.p. (SA-I) 112°C.

(4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenyl)methyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarboxy)benzoate.

[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenyl]-methyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarboxy)-benzoate.

20 [4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenyl]-methyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarboxy)benzoate.

[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenyl]-methyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarboxy)benzoate.

[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenyl]-methyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarboxy)-benzoate.

[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenyl]-methyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)-benzoate.

30 [4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenyl]-methyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarboxy)-benzoate.

### Example 2

0.6 g of 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarboxy)-benzoic acid and 0.4 g of (4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethanol, 0.04 g of 4-dimethylaminopyridine, 0.2 g N,N'-dicyclodicyclohexyldicarbodiimide and 20 ml of dichloromethane are reacted in an analogous manner to

Example 1 to give (4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethyl 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarboxy)benzoate.

5        The (4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethanol used as the starting material is prepared as follows:

10        a)    0.6 g of 4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoic acid and 0.2 g of (4-hydroxyphenoxy)ethanol, 0.04 g of 4-dimethylaminopyridine, 0.4 g of N,N'-dicyclodicyclohexyldicarbodiimide and 50 ml of dichloromethane are reacted in an analogous manner to Example 1 to give 0.4 g of (4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethanol.

15        b)    A solution of 5.0 g of 4-hydroquinone and 3.7 g of chloroethanol in 50 ml of ethyl methyl ketone is treated with 25 g of finely powdered potassium carbonate and the mixture is heated under slight reflux overnight. The suspension is suction  
20        filtered and the filtrate is concentrated in a vacuum. A solution of the residue in 100 ml of diethyl ether is washed twice with 100 ml of water each time, dried over sodium sulphate and concentrated. Chromatography of the crude product on silica gel with hexane/ethyl acetate (vol. 7:3) gives 2.0 g of (4-hydroxy-  
25        phenoxy)ethanol.

The following compounds can be produced in an analogous manner:

30        (4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarboxy)benzoate.

35        (4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarboxy)benzoate.

(4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarboxy)benzoate.

(4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarboxy)benzoate.

5 (4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate.

(4-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenoxy)ethyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarboxy)benzoate.

10 [4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenoxy]ethyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarboxy)benzoate.

[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenoxy]ethyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarboxy)benzoate.

15 [4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenoxy]ethyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarboxy)benzoate.

[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenoxy]ethyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarboxy)benzoate.

[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenoxy]ethyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate.

25 [4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]benzoyloxy)phenoxy]ethyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarboxy)benzoate.

### Example 3

30

0.3 g of 4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoic acid, 0.8 g of 4-hydroxybutyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate and 0.04 g of 4-dimethylaminopyridine, 0.2 g N,N'-dicyclodicyclohexyldicarbodiimide and 50 ml of dichloromethane are reacted in an analogous manner to Example 1 to give 0.5 g of 4-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]butyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate.

The 4-hydroxybutyl 2,5-bis(4-[11-acryloyloxyundecyloxy]-phenylcarboxy)benzoate used as the starting material is prepared as follows:

5

(a) 1.0 g of 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoic acid and 1.0 g of 1,4-butanediol, 0.04 g of 4-dimethylaminopyridine, 0.4 g of N,N'-dicyclodicyclohexyldicarbodiimide and 50 ml of dichloromethane are reacted in an analogous manner to Example 1 to give 0.8 g of 4-hydroxybutyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate.

10

The following compounds can be produced in an analogous manner:

15

3-[4-(2-Amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]propyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

20

5-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]pentyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

6-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]hexyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

25

7-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]heptyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

8-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]octyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

30

9-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]nonyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

10-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]decyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

35

11-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]undecyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

12-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]dodecyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarboxy)benzoate;

3-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]propyl 2,5-bis(4-[5-acryloyloxypropyloxy]phenylcarboxy)benzoate;

3-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]propyl 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarboxy)benzoate;

3-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]propyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarboxy)benzoate;

3-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]propyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarboxy)benzoate;

3-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]propyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarboxy)benzoate;

3-[4-(2-amino-5-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]propyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarboxy)benzoate;

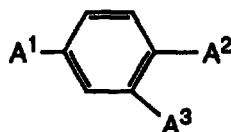
#### Example 4

A mixture (I-N\*, 114°C, N\*-Sc\* 106°C and Sc\*-Sx 70°C) of 0.05 g of 4-[4-(5-amino-2-nitro-4-[(S)-2-octyloxy]phenyl)benzoyloxy]phenylmethyl 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarboxy)benzoate and 0.20 g of 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarboxy)benzoate provided with 6  $\mu$ m spacer was treated with 3 wt.% of a photoinitiator (Irgacure, Ciba Geigy) and 1 wt.% of BHT and filled at 160°C into a 7.8  $\mu$ m cell with parallel orientation. The layer was orientated at 105°C in an electric field (15 V ac), then the helix was wound up at 90°C and at 110 V dc and illuminated in this state with xenon light (e.g. for 15 minutes). This layer functions as a frequency doubler.



## Claims

1. Compounds of the general formula



5

I

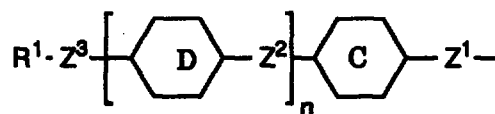
wherein

A<sup>1</sup>, A<sup>2</sup> each independently signify a cross-linkable mesogenic residue and

10 A<sup>3</sup> signifies an optically active, mesogenic residue.

2. Compounds according to claim 1, wherein the cross-linkable, mesogenic residues A<sup>1</sup> and A<sup>2</sup> are the same and signify residues of the formula

15



II

wherein

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

25 Z<sup>1</sup> signifies a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-, -COO-, -OOC-, -(CH<sub>2</sub>)<sub>4</sub>- or -(CH<sub>2</sub>)<sub>3</sub>O-;

Z<sup>2</sup> signifies a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -COO-, -OOC-, -(CH<sub>2</sub>)<sub>4</sub>-, -O(CH<sub>2</sub>)<sub>3</sub>- or -(CH<sub>2</sub>)<sub>3</sub>O-;

30 Z<sup>3</sup> signifies -(CH<sub>2</sub>)<sub>m</sub>-, -(CH<sub>2</sub>)<sub>m</sub>O-, -(CH<sub>2</sub>)<sub>m</sub>COO- or -(CH<sub>2</sub>)<sub>m</sub>OOC-;

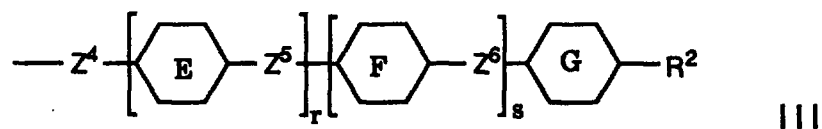
n signifies 0 or 1;

m signifies a whole number of 1 to 16; and

R<sup>1</sup>

signifies a cross-linkable group such as acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyl ether, vinyl ester, styrene derivative, maleic acid derivative or fumaric acid derivative or a cinnamic acid derivative, which is optionally substituted with methyl, methoxy, cyano and/or halogen.

3. Compounds according to claim 1 or 2, wherein the optically active mesogenic residue A<sup>3</sup> signifies a residue of the formula



wherein

rings E and F

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

ring G

signifies 1,4-phenylene, which is unsubstituted or mono- or disubstituted with halogen, methyl, dimethylamino, amino, nitro and/or cyano;

Z<sup>4</sup>

signifies a single bond,  $\text{---(CH}_2\text{)}_p\text{---}$ ,  $\text{---(CH}_2\text{)}_p\text{O---}$ ,  $\text{---O(CH}_2\text{)}_p\text{---}$ ,  $\text{---(CH}_2\text{)}_p\text{COO---}$ ,  $\text{---OOC(CH}_2\text{)}_p\text{---}$ ,  $\text{---(CH}_2\text{)}_p\text{OOC---}$ ,  $\text{---COO(CH}_2\text{)}_p\text{---}$ ,  $\text{---OOC(CH}_2\text{)}_p\text{OOC---}$ ,  $\text{---O(CH}_2\text{)}_p\text{OOC---}$  or  $\text{---COO(CH}_2\text{)}_p\text{O---}$ ;

Z<sup>5</sup>, Z<sup>6</sup>

signify a single bond,  $\text{---CH}_2\text{CH}_2\text{---}$ ,  $\text{---CH}_2\text{O---}$ ,  $\text{---OCH}_2\text{---}$ ,  $\text{---COO---}$ ,  $\text{---OOC---}$ ,  $\text{---(CH}_2\text{)}_4\text{---}$ ,  $\text{---O(CH}_2\text{)}_3\text{---}$  or  $\text{---(CH}_2\text{)}_3\text{O---}$ ;

p

signifies a whole number of 1 to 16;



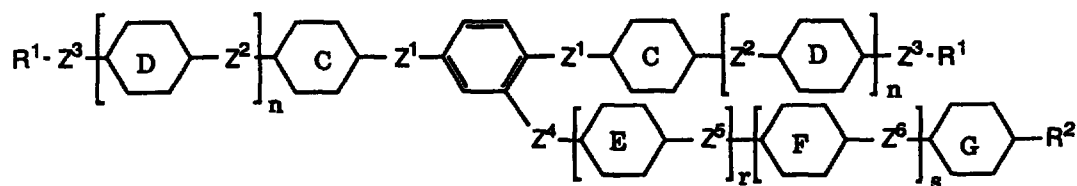
r, s  
R<sup>2</sup>

signify 0 or 1; and  
signifies an optically active group such as  
(S)- or (R)-2-butyloxy, (S)- or (R)-2-  
pentyloxy, (S)- or (R)-2-hexyloxy, (S)- or  
(R)-2-heptyloxy, (S)- or (R)-2-octyloxy or  
alkyl, alkoxy or alkanoyloxy with 4 to 8  
carbon atoms, which is substituted with  
methyl, methoxy, cyano and/or halogen.

5

10

4. Compounds according to claim 1 of the formula



I-1

15

wherein  
rings C and D

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

20

rings E and F

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

25

ring G

signifies 1,4-phenylene, which is unsub-  
stituted or mono- or disubstituted with  
halogen, methyl, dimethylamino, amino,  
nitro and/or cyano;

30

Z<sup>1</sup>

signifies a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-,  
-COO-, -OOC-, -(CH<sub>2</sub>)<sub>4</sub>- or -(CH<sub>2</sub>)<sub>3</sub>O-;

Z<sup>2</sup>, Z<sup>5</sup>, Z<sup>6</sup>

each independently signify a single bond,  
-CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O-,

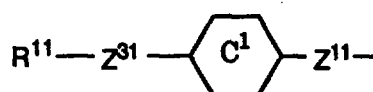
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|    |                |                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
|----|----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|    |                | -OCH <sub>2</sub> -, -COO-, -OOC-, -(CH <sub>2</sub> ) <sub>4</sub> -, -O(CH <sub>2</sub> ) <sub>3</sub> -<br>or -(CH <sub>2</sub> ) <sub>3</sub> O-;                                                                                                                                                                                                                                                                                                   |
|    | Z <sup>3</sup> | signifies -(CH <sub>2</sub> ) <sub>m</sub> -, -(CH <sub>2</sub> ) <sub>m</sub> O-,<br>-(CH <sub>2</sub> ) <sub>m</sub> COO- or -(CH <sub>2</sub> ) <sub>m</sub> OOC-;                                                                                                                                                                                                                                                                                   |
| 5  | Z <sup>4</sup> | signifies a single bond, -(CH <sub>2</sub> ) <sub>p</sub> -,<br>-(CH <sub>2</sub> ) <sub>p</sub> O-, -O(CH <sub>2</sub> ) <sub>p</sub> -, -(CH <sub>2</sub> ) <sub>p</sub> COO-,<br>-OOC(CH <sub>2</sub> ) <sub>p</sub> -, -(CH <sub>2</sub> ) <sub>p</sub> OOC-, -COO(CH <sub>2</sub> ) <sub>p</sub> -,<br>-OOC(CH <sub>2</sub> ) <sub>p</sub> OOC-, -O(CH <sub>2</sub> ) <sub>p</sub> OOC- or<br>-COO(CH <sub>2</sub> ) <sub>p</sub> O-;              |
| 10 | n              | signifies 0 or 1;                                                                                                                                                                                                                                                                                                                                                                                                                                       |
|    | m,p            | signify a whole number from 1 to 16;                                                                                                                                                                                                                                                                                                                                                                                                                    |
|    | r,s            | signify 0 or 1;                                                                                                                                                                                                                                                                                                                                                                                                                                         |
|    | R <sup>1</sup> | signifies a cross-linkable group such as<br>acrylate, methacrylate, 2-chloroacrylate,<br>15 2-phenylacrylate, acryloylphenylene,<br>acrylamide, methacrylamide, 2-<br>phenylacrylamide, epoxy, itaconic acid<br>ester, vinyl ether, vinyl ester, styrene<br>20 derivative, maleic acid derivative or<br>fumaric acid derivative or a cinnamic acid<br>derivative, which is optionally substituted<br>with methyl, methoxy, cyano and/or<br>halogen; and |
|    | R <sup>2</sup> | signifies an optically active group such as<br>25 (S)- or (R)-2-butyloxy, (S)- or (R)-2-<br>pentyloxy, (S)- or (R)-2-hexyloxy, (S)- or<br>(R)-2-heptyloxy, (S)- or (R)-2-octyloxy or<br>alkyl, alkoxy or alkanoyloxy with 4 to 8<br>30 carbon atoms, which is substituted with<br>methyl, methoxy, cyano and/or halogen.                                                                                                                                |

5. Compounds according to claim 1 or 2, wherein the mesogenic residues A<sup>1</sup> and A<sup>2</sup> are the same and signify residues of the formula

35



II-a



wherein

$R^{11}$  signifies acrylate, methacrylate or epoxy;

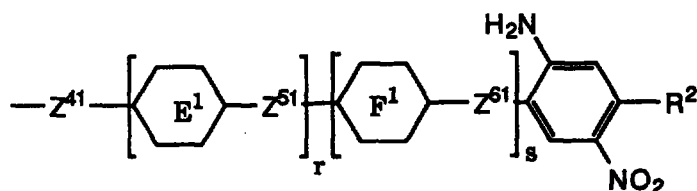
$Z^{31}$  signifies  $-(CH_2)_t-$ ,  $-(CH_2)_tO-$ ,  $-(CH_2)_tCOO-$  or  $-(CH_2)_tOOC-$ ;

5  $t$  signifies a whole number from 4 to 12;

ring  $C^1$  signifies 1,4-phenylene, 2-fluoro-1,4-phenylene or, 3-fluoro-1,4-phenylene; and

$Z^{11}$  signifies  $-CH_2O-$ ,  $-COO-$  or  $-OOC-$ .

- 10 6. Compounds according to claim 1 or 3, wherein the optically active, mesogenic residue  $A^3$  signifies a residue of the formula



III-a

15

wherein

$R^2$  signifies (S)- or (R)-2-butyloxy, (S)- or (R)-2-pentyloxy, (S)- or (R)-2-hexyloxy, (S)- or (R)-2-heptyloxy or (S)- or (R)-2-octyloxy;

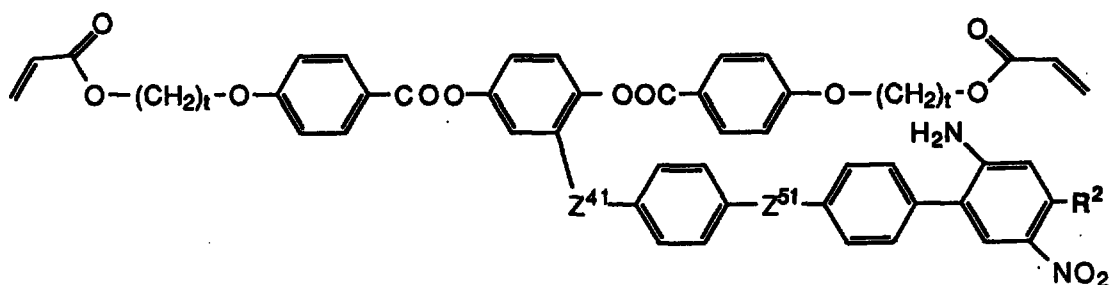
20  $r, s$  signify 0 or 1;

$Z^{41}$  signify  $-CH_2CH_2CH_2-$ ,  $-OCH_2CH_2-$ ,  $-CH_2CH_2O-$ ,  $-COOCH_2-$  or  $-CH_2OOC-$ ;

$Z^{51}, Z^{61}$  signify a single bond,  $-CH_2CH_2-$ ,  $-CH_2O-$ ,  $-COO-$ ,  $-OOC-$ ,  $-(CH_2)_4-$  or  $-(CH_2)_3O-$ ; and

25 rings  $E^1$  and  $F^1$  signify 1,4-phenylene.

7. Compounds of the formula





wherein

t is a whole number from 4 to 12;

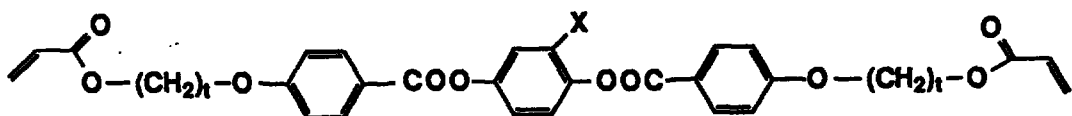
R<sup>2</sup> signifies (S)- or (R)-2-butyloxy, (S)- or (R)-2-pentyloxy, (S)- or (R)-2-hexyloxy, (S)- or (R)-2-heptyloxy or (S)- or (R)-2-octyloxy;

Z<sup>41</sup> signifies -COOCH<sub>2</sub>-; and

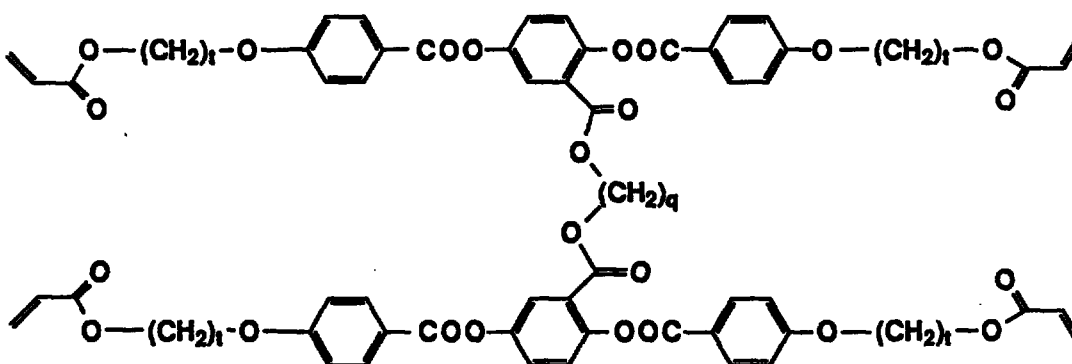
Z<sup>51</sup> signifies a single bond, -COO- or -OOC-.

8. Cross-linkable, liquid crystalline mixtures consisting of at least two components, of which at least one component is a compound of formula I defined in claim 1.

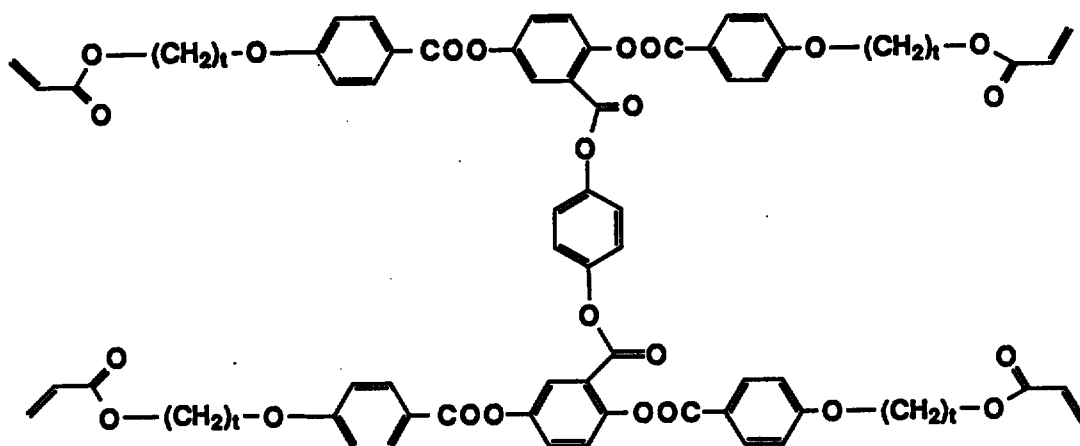
9. Cross-linkable, liquid crystalline mixtures according to claim 8, which contain, in addition to one or more compounds of formula I, one or more compounds from the group of compounds of the formulae



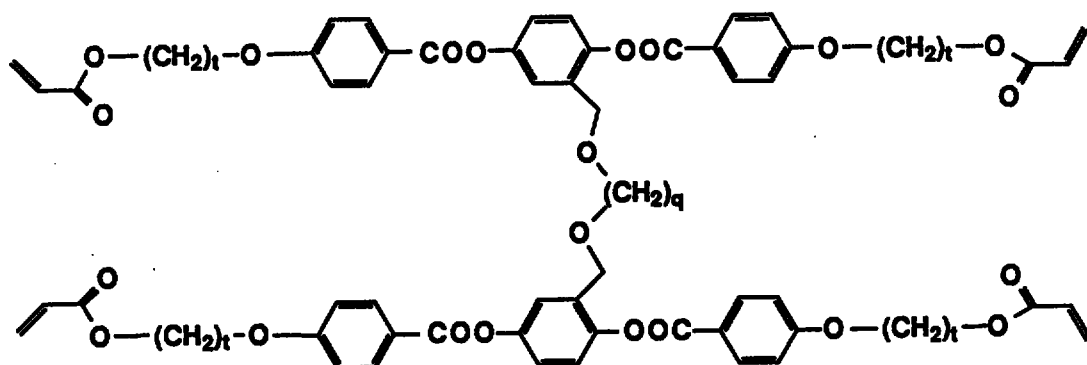
V



VI

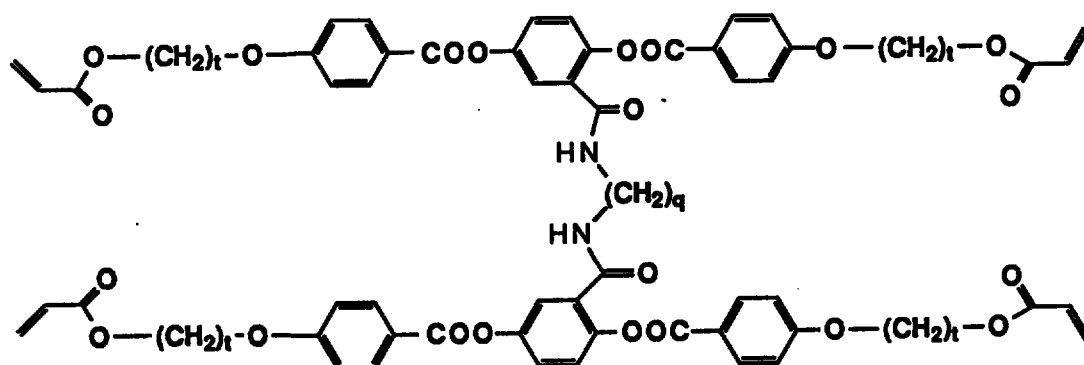


VII

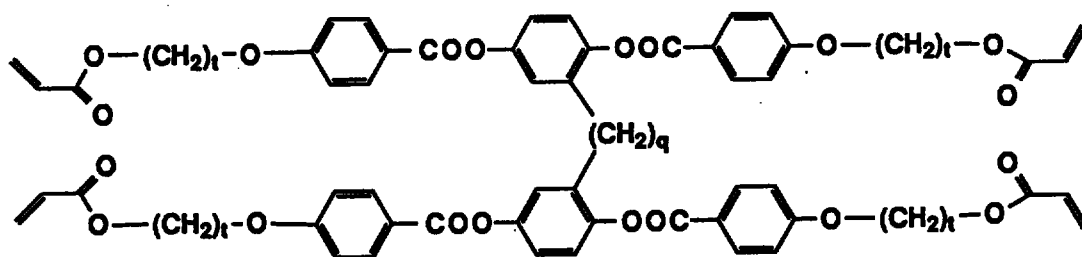


VIII

5



IX



X

10



wherein t signifies a whole number from 4 to 12 and q signifies a whole number from 2 to 12.

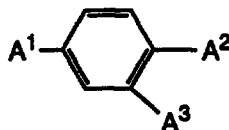
10. The use of compounds according to any one of claims 1  
5 to 7 in their cross-linked state for optical components.

11. The use of cross-linkable liquid crystalline mixtures according to claim 8 or 9 in their cross-linked state for optical components.

# Optically active smectic photo-cross-linkable Liquid Crystals

## Abstract

The present invention is concerned with optically active, ferroelectric, smectic, photo-cross linkable compounds of the formula



I

wherein

A<sup>1</sup>, A<sup>2</sup> each independently signify a cross-linkable mesogenic residue and

A<sup>3</sup> signifies an optically active, mesogenic residue,

as well as liquid crystalline mixtures which contain such compounds and their use in the cross-linked state in optical components.