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REPLACEDRef. 6220/126

- 5 The present invention is concerned with photo cross-linkable liquid crystalline 1,2-phenylene derivatives, 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 an appropriate 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, etc. can be produced. Such optical components can be used, for example, for frequency doubling (SHG) or in colour
- 20 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 optical filters should have a strong absorption in a direction perpendicular to the filter surface.

In addition to the general interest in photo cross-linkable liquid crystals for optical components, such liquid crystalline

30 materials are suitable as a cladding for glass fibres for optical data transmission. The use of such materials increases the elastic modulus in the longitudinal axis of the fibre, lessens the thermal expansion coefficients and thus reduces 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 usual solvents 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.

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

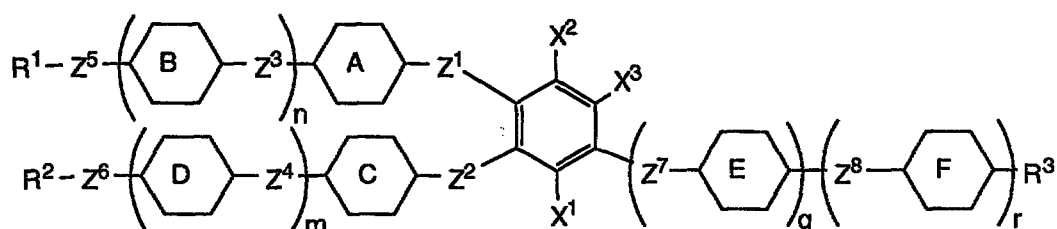
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There is accordingly the need, for use in optical components, optical filters, channel waveguides, Mach-Zehnder structures, homeotropic layers, etc., to produce photochemically oligomerisable or polymerisable compounds which are
30 distinguished by an especially high optical anisotropy Δn . They should have low melting points and clearing points in order that the viscosity at normal processing temperatures in the liquid crystalline state is not too high. Further, they should be orientable and structurable as domain-free as possible and should
35 also have an excellent thermal stability and long-term stability in the cross-linked state. Moreover, especially for channel waveguides, Mach-Zehnder structures, homeotropic layers, etc., they should have a positive dielectric anisotropy and be capable of

orientation in an electric field. This permits, for example, the additional structuring by the use of electrodes of photochemically oligomerisable or polymerisable compounds which are already oriented homogeneously by an orienting layer.

- 5 Conventional photochemically oligomerisable or polymerisable liquid crystals usually have a negative or a very weak positive dielectric anisotropy.

The present invention now provides compounds which are
10 outstandingly suitable as single components or as components of liquid crystal mixtures for the aforementioned uses. The object of the present invention are compounds of general formula I



15

I

wherein

rings A - F

20

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

25

Z¹, Z² and Z⁷

independently of one another signify -CH₂-(CH₂)_s-, -(CH₂)_sO-, -O(CH₂)_s-, -COO-, -OOC-, -(CH₂)_sCOO- or -(CH₂)_sOOC-;

Z³, Z⁴ and Z⁸

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independently of one another signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;

Z⁵ and Z⁶

35

signify -(CY₂)_s-, -O(CY₂)_s-, -(CY₂)_sO-, -(CY₂)_sCOO-, -(CY₂)_sOOC-, -(Si[(CH₃)₂]O)_s-, -OCH₂(Si[(CH₃)₂]O)_sSi[(CH₃)₂]CH₂O- or -NHCH₂(Si[(CH₃)₂]O)_sSi[(CH₃)₂]CH₂NH-;

- Y signifies hydrogen or fluorine;
 m, n, q and r independently of one another signify 0, 1 or 2;
 s signifies a whole number of 1 to 16;
 5 R¹ and R² signify cross-linkable groups 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-,
 10 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-,

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

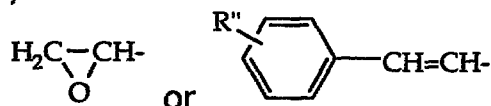
 15 Ph signifies phenyl;
 R' signifies lower alkyl;
 R'' signifies methyl, methoxy, cyano or halogen, with the proviso that R¹-Z⁵ and R²-Z⁶ contain no -O-O- or -N-O- groups;
 20 R³ signifies hydrogen, halogen, cyano or an alkyl, alkoxy, alkoxycarbonyl or alkanoyl-oxy group optionally substituted with methoxy, cyano and/halogen; and
 25 X¹, X² and X³ independently signify hydrogen, halogen, cyano or lower alkyl,

whereby the two rings B and D can be the same or different when m is 2 and/or n is 2.

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

Preferably, the cross-linkable group R¹ signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-, CH₂=C(Cl)-COO-, CH₂=C(Ph)-COO-, CH₂=CH-COO-Ph- CH₂=CH-CONH-, CH₂=C(CH₃)-CONH-, CH₂=C(Ph)-CONH-, CH₂=CH-O-, CH₂=CH-OOC-, -cis,trans -HCOO-CR'=CR'-COO-

5



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

10

These are the 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 $\begin{array}{c} \text{H}_2\text{C}-\text{CH}- \\ \diagup \quad \diagdown \\ \text{O} \end{array}$.

Hydrogen, fluorine, chlorine, cyano and methyl are especially preferred groups X¹, X² and X³.

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 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- 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 in the scope of the present invention fluorine, chlorine or bromine, especially fluorine;

35

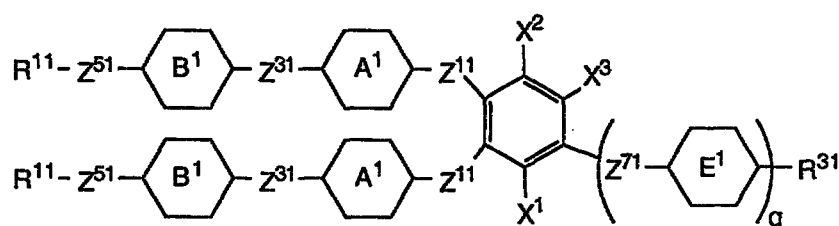
"alkyl, alkoxy, alkoxycarbonyl or alkanoyloxy group optionally substituted with methoxy, cyano and/or halogen" embraces in the scope of the present invention groups in which the

alkyl residue can be straight-chain or branched and preferably has 1 to 12 carbon atoms. The groups can be mono- or multiply-substituted with methoxy, cyano and/or fluorine, chlorine or bromine. Particularly preferred groups are methyl, ethyl, propyl, butyl, pentyl, methoxy, ethoxy, propyloxy, butoxy, acyloxy, propanoyloxy, butanoyloxy, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, trifluoromethyl, trifluoromethoxy, 2,2,2-trifluoroethoxy, trifluoroacetyloxy, chlorodifluoromethoxy, 2-cyanoethyl, 2-fluoroethyl, 2-chloroethyl, 2-bromoethyl, 2-methoxyethoxy, 2,2-difluoroethyl, 2,2,2-trifluoroethyl and the like;

"lower alkyl" embraces in the scope of the present invention 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.

The mesophase type of the compounds in accordance with the invention can be influenced by varying the rings in the side-chains. 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.

Preferred compounds have general formula I-A



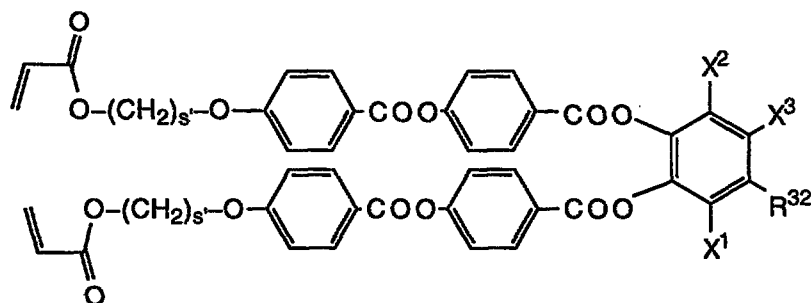
I - A

wherein
 A¹, B¹ and E¹ independently of one another signify 1,4-phenylene optionally substituted with fluorine, pyridine-2,5-diyl, pyrimidine-2,5-diyl or trans-1,4-cyclohexylene;

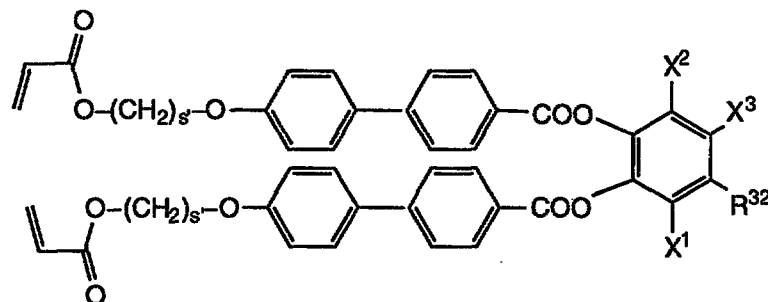
	Z ¹¹	signifies -CH ₂ CH ₂ -, -CH ₂ O-, -COO-, -OOC-, -(CH ₂) ₄ - or -(CH ₂) ₃ O-;
	Z ³¹	signifies a single bond, -CH ₂ O-, -COO- or -OOC-;
5	Z ⁵¹	signifies -(CH ₂) _{s'} -, -(CH ₂) _{s'} O-, -(CH ₂) _{s'} COO- or -(CH ₂) _{s'} OOC-;
	Z ⁷¹	signifies -CH ₂ O- or -COO- ;
	s'	signifies a whole number of 3 to 12;
	R ¹¹	signifies CH ₂ =CH-COO-, CH ₂ =C(CH ₃)-COO-, CH ₂ =CH-O- or $\begin{matrix} \text{H}_2\text{C} & \text{CH-} \\ & \diagdown \quad \diagup \\ & \text{O} \end{matrix}$
10	R ³¹	signifies halogen, cyano, lower alkyl or alkoxycarbonyl;
	q	signifies 0 or 1 and
15	X ¹ , X ² and X ³	have the significance given under formula I.

Particularly preferred are compounds of formula I-A in
which q is 0, such as, for example, compounds of general formulae
Ia-Ic

20



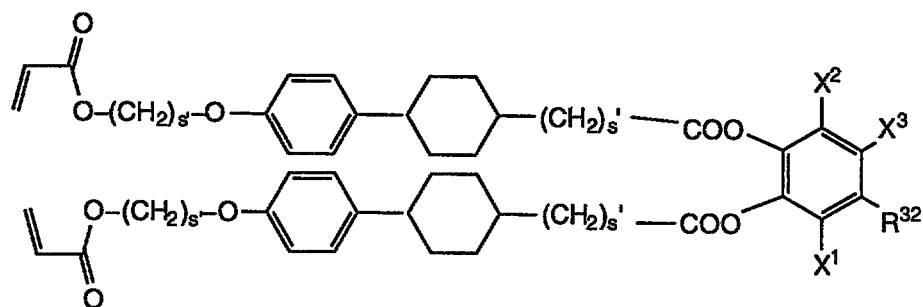
I - a



I - b

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8

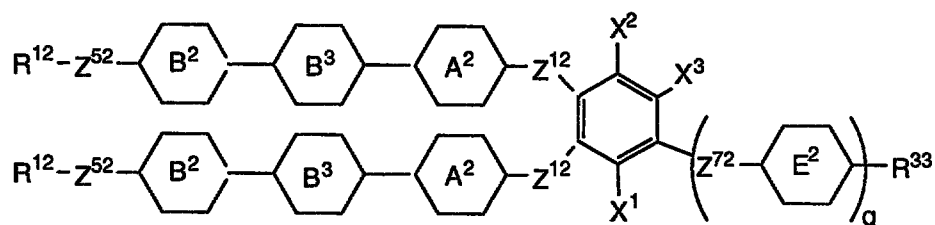


I - c

5 wherein R³² signifies fluorine, chlorine, cyano or alkoxycarbonyl; and the remaining symbols are as defined above.

Compounds of formula I-a in which R³² signifies cyano or alkoxycarbonyl and X¹, X² and X³ signify hydrogen are particularly
10 preferred.

Also preferred are compounds of formula I-B



I - B

wherein

A², B², B³ and E² independently of one another signify 1,4-phenylene optionally substituted with fluorine or trans-1,4-cyclohexylene;

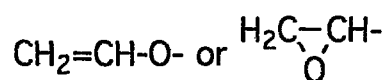
20 Z¹² signifies -(CH₂)₂COO-, -(CH₂)_{s'}COO- or -(CH₂)_{s'}O-;

Z⁵² signifies -(CH₂)_{s'}-, -(CH₂)_{s'}O-, -(CH₂)_{s'}COO- or -(CH₂)_{s'}OOC-;

Z⁷² signifies -CH₂O- or -COO- ;

25 s' signifies a whole number of 3 to 12;

R¹² signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-,

R³³

signifies halogen, cyano or alkoxycarbonyl;

q

signifies 0 or 1;

X¹, X² and X³

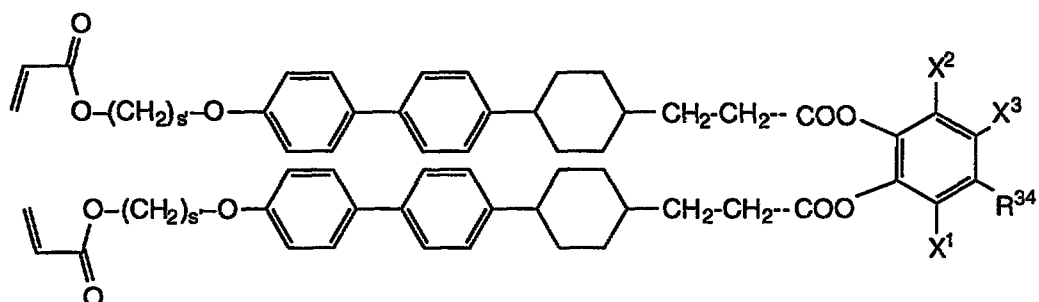
have the significance given under formula

I.

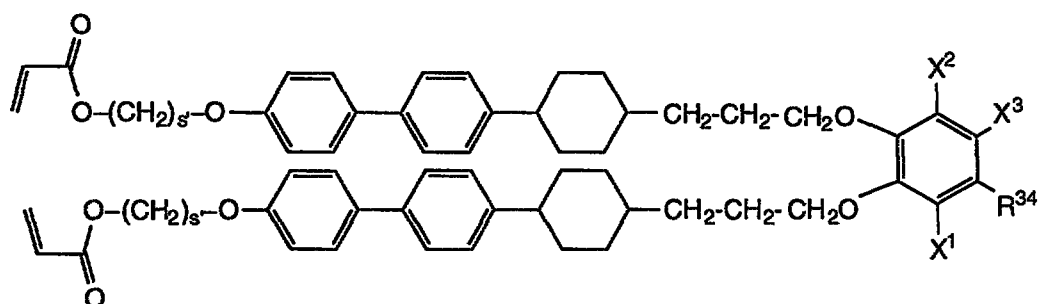
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Particularly preferred are compounds of formula I-B in which q is 0, such as, for example, compounds of general formulae Id-Ig

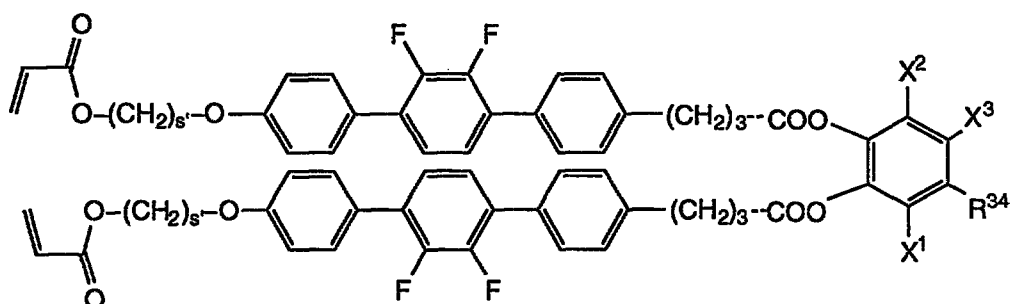
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I - d

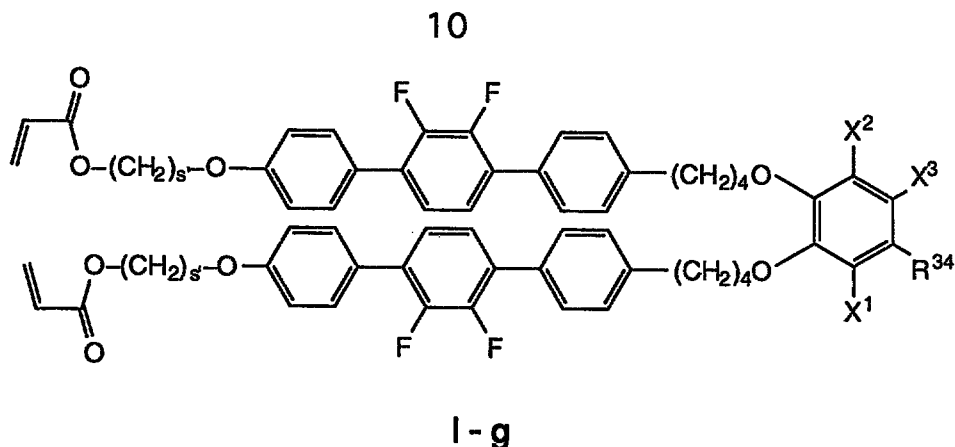


I - e



I - f

15



5 wherein R^{34} signifies fluorine, chlorine, cyano or alkoxy-carbonyl; and the remaining symbols are as defined above.

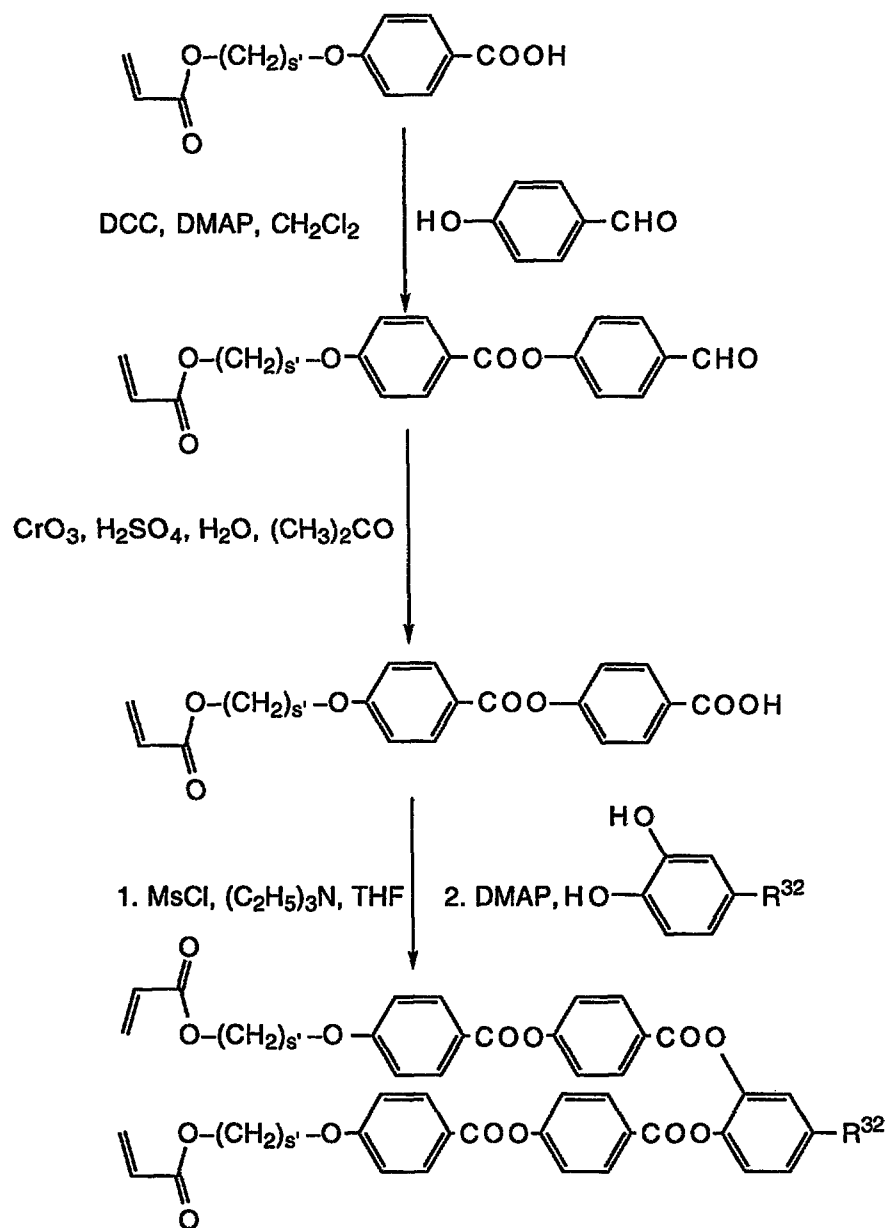
10 The compounds of formulae I-A and I-B are very readily accessible synthetically and can be produced, for example, analogously to the methods illustrated in Schemes 1 to 10. Thus, 2-hydroxyphenols can be reacted with (ω -acryloyloxyalkyloxy)-substituted carboxylic acids in a manner known per se. This esterification can be effected, for example, via the corresponding methanesulphonic acid ester in tetrahydrofuran or in the presence of N,N'-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridine (DMAP) in dichloromethane or another suitable solvent

15 such as e.g. chloroform. The 2-hydroxyphenols can also be reacted in a Mitsunobu reaction with (ω -acryloyloxyalkyloxy)-substituted benzyl alcohols. This etherification can be effected, for example, at room temperature in the presence of diethyl azodicarboxylate and triphenylphosphine in tetrahydrofuran or another suitable

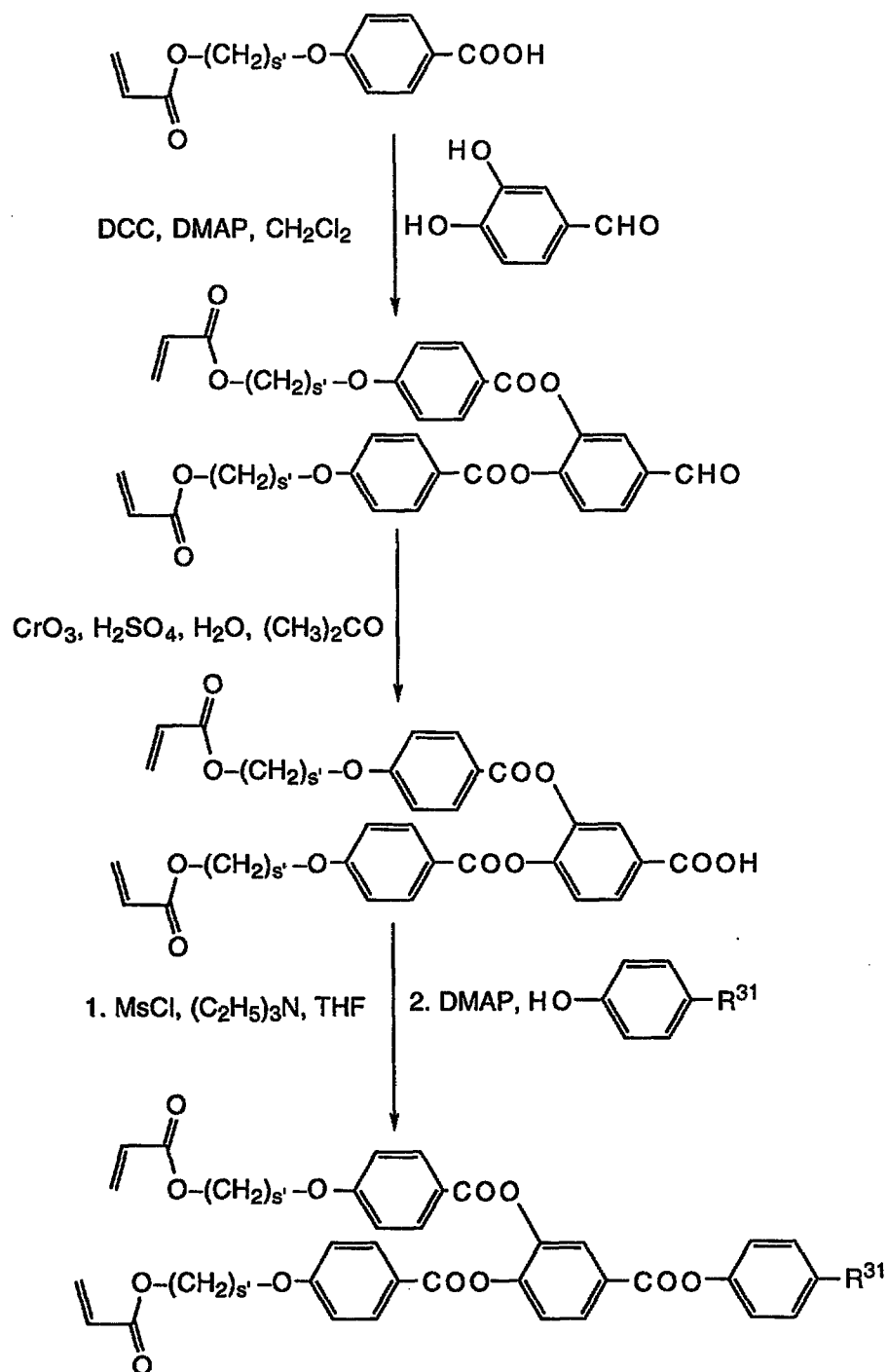
20 solvent such as e.g. N,N'-dimethylformamide. The 2-hydroxyphenols are known or can be prepared according to methods known to a person skilled in the art.

25 In the Schemes the symbols have the aforementioned significances.

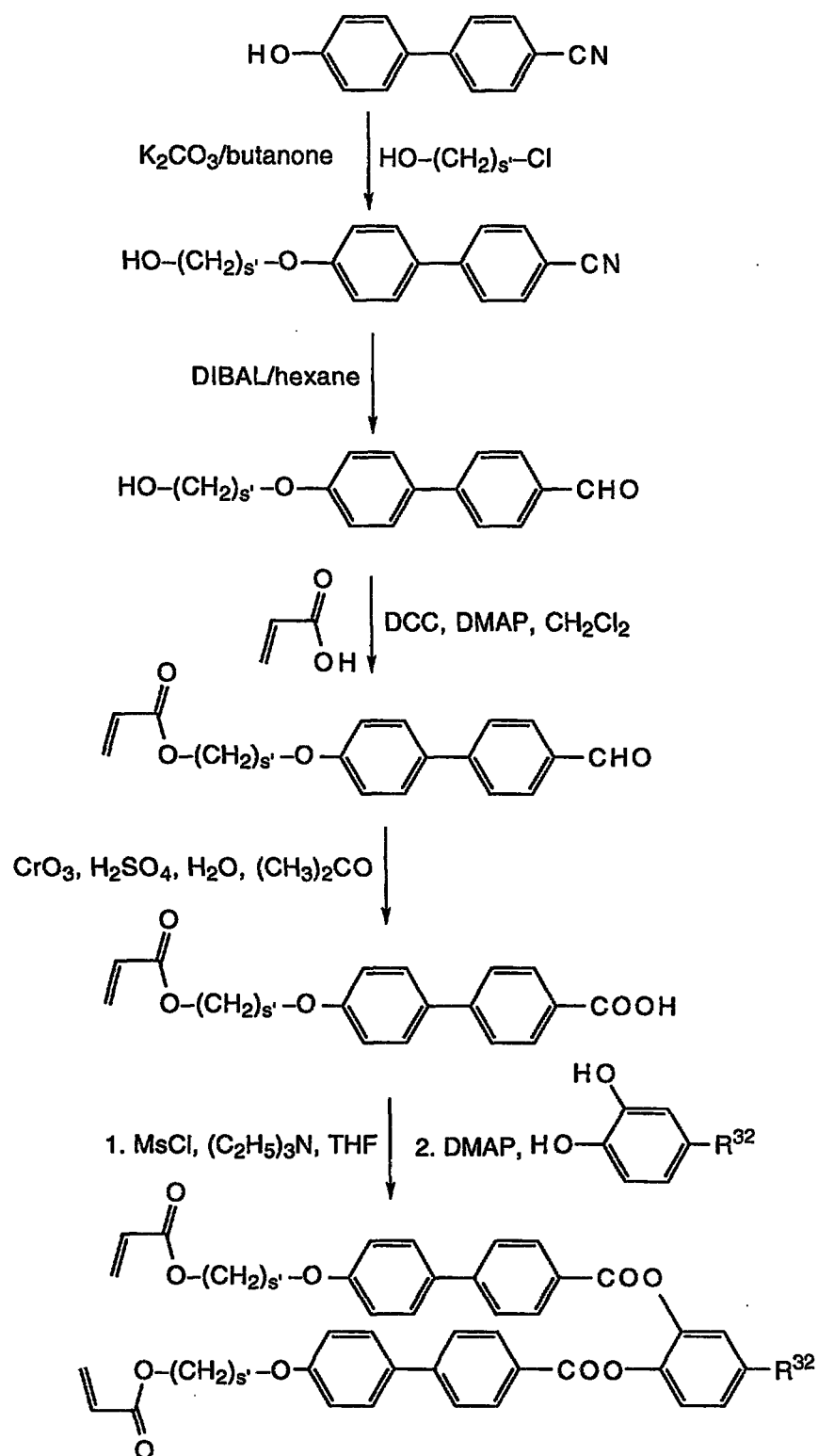
Scheme 1



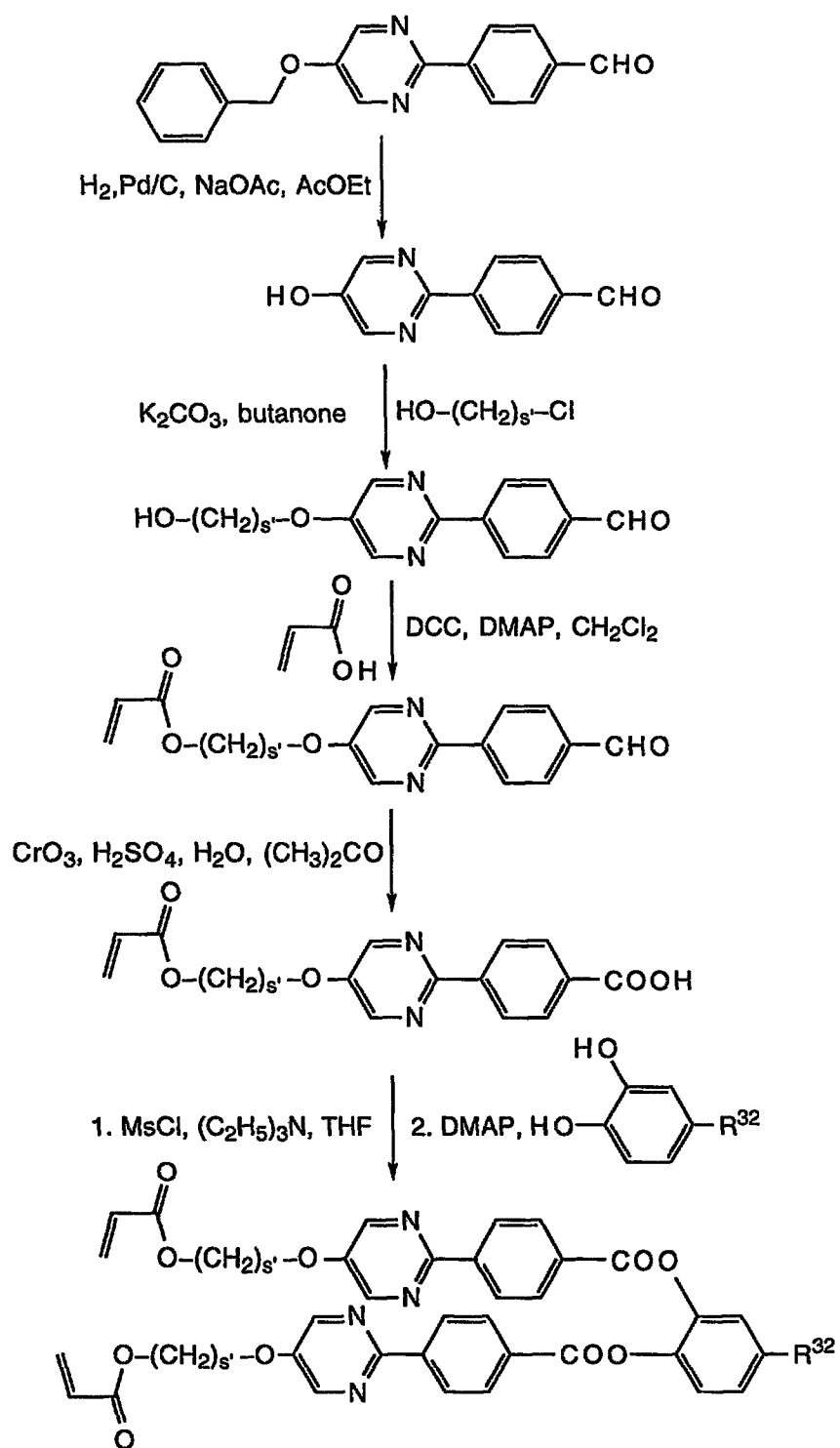
Scheme 2



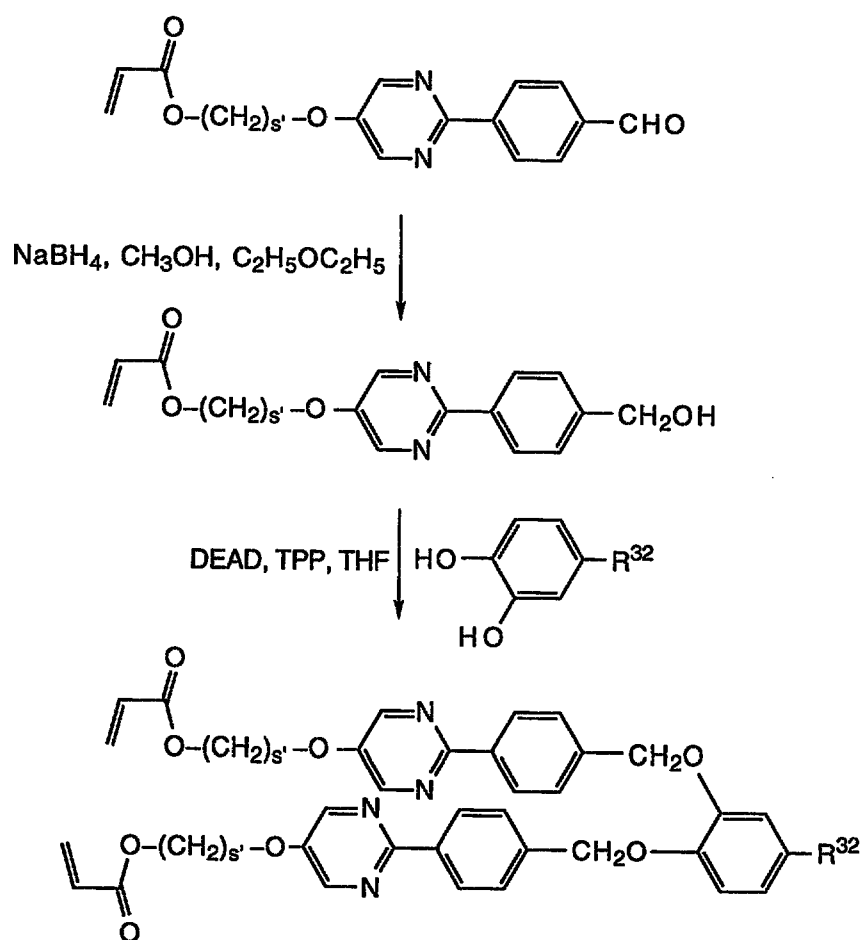
Scheme 3



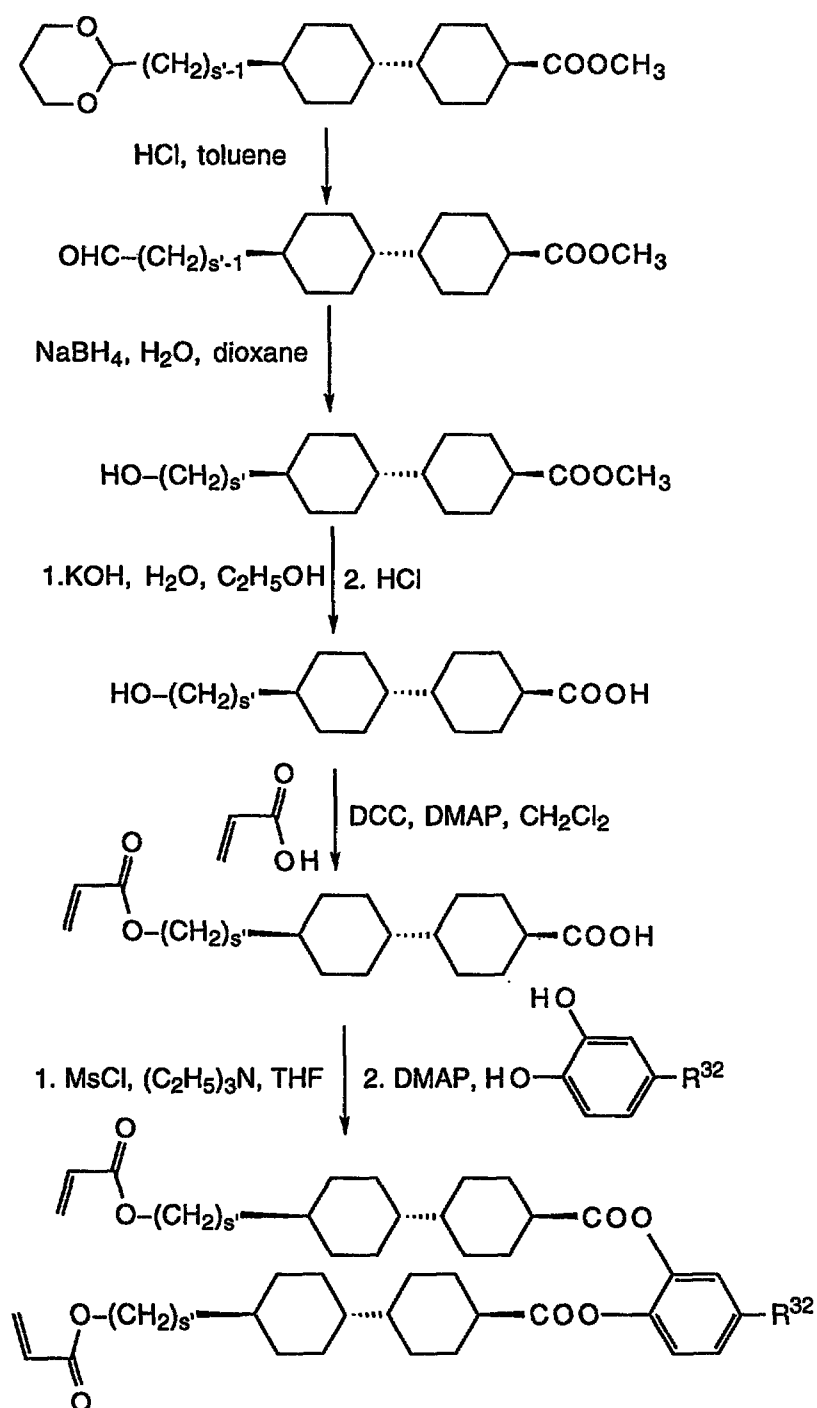
Scheme 4



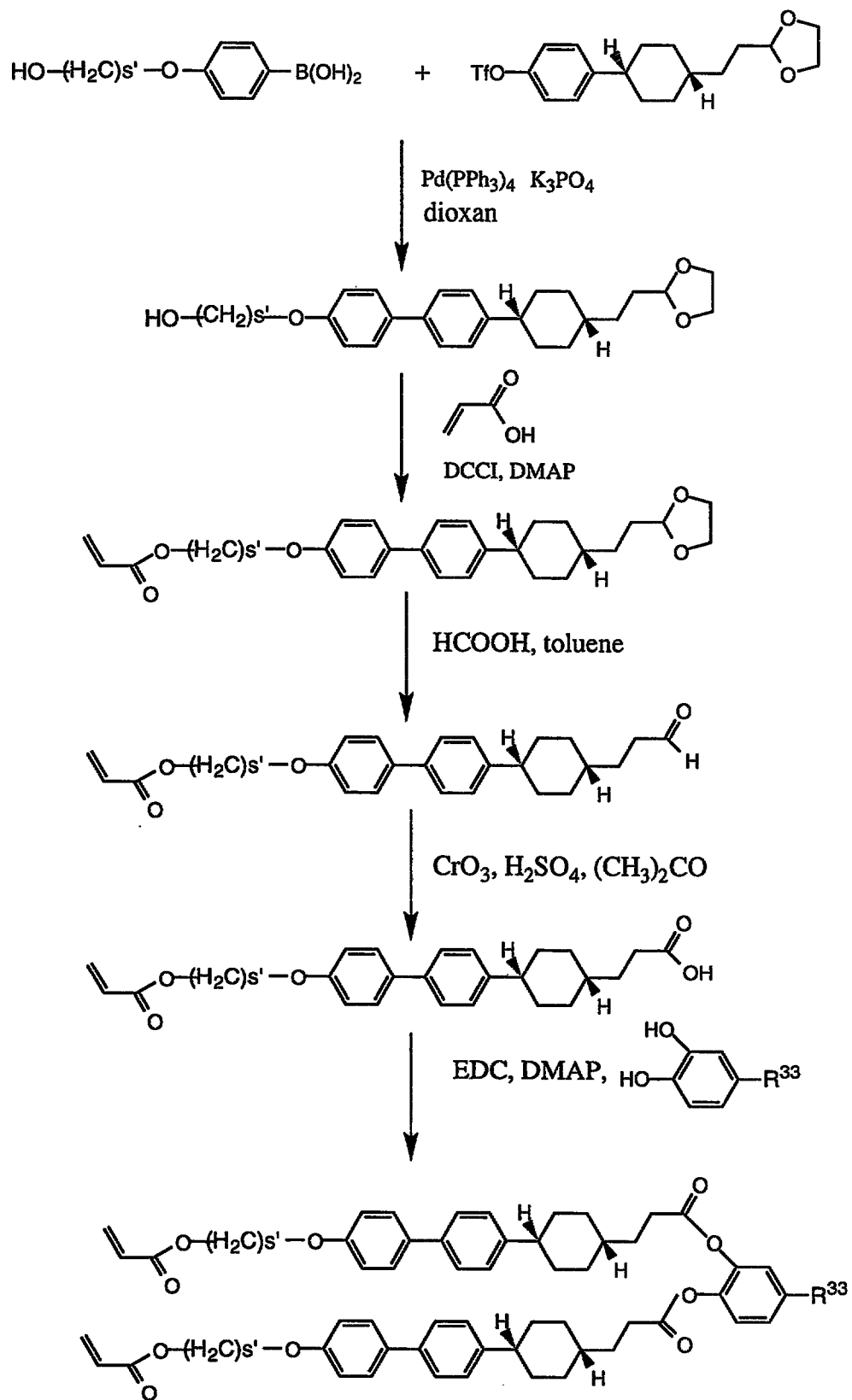
Scheme 5



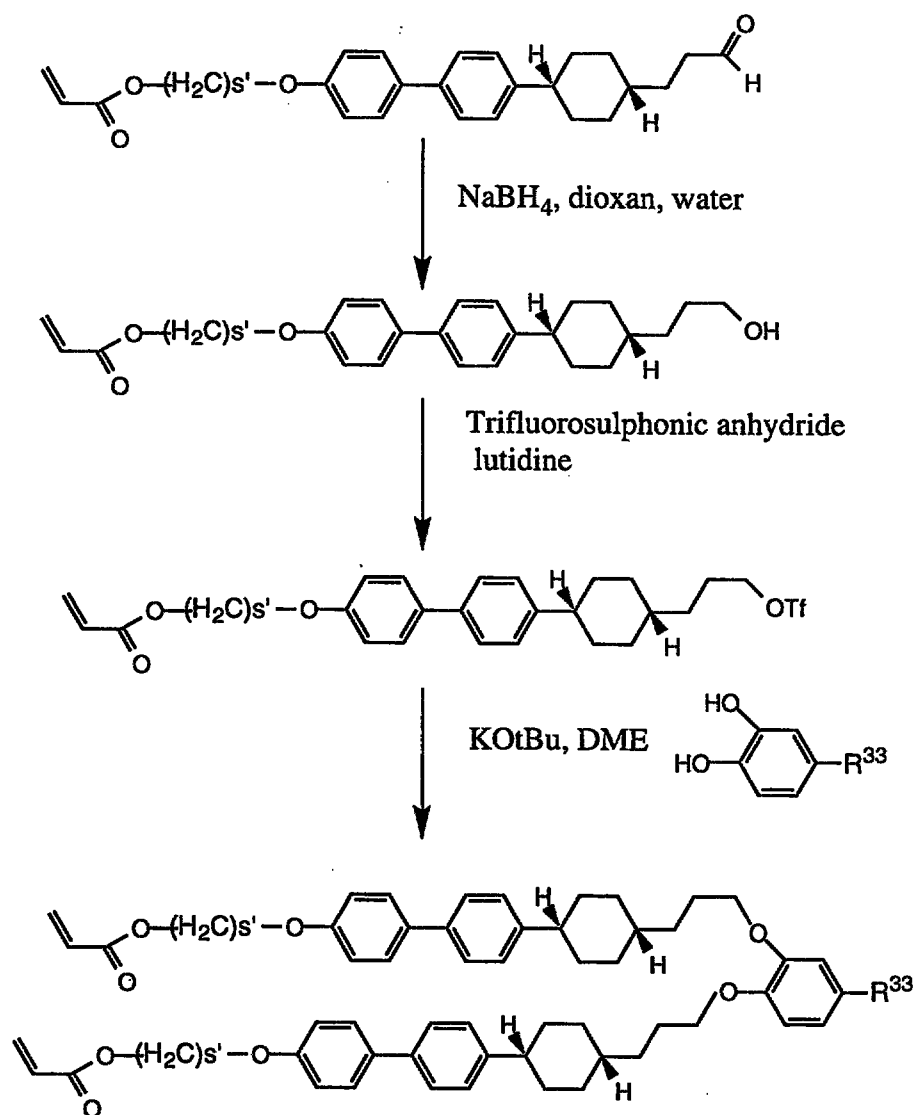
Scheme 6



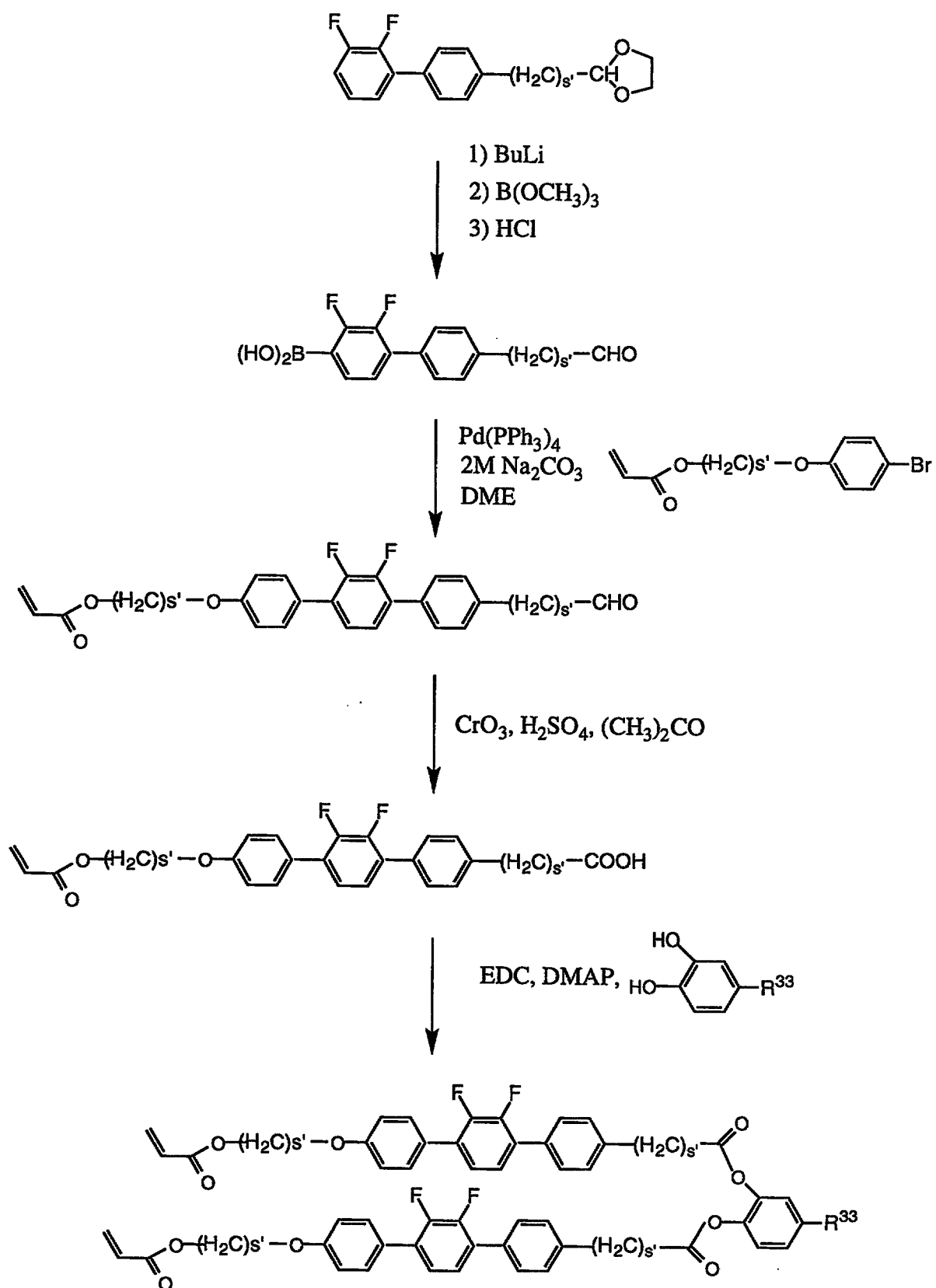
Scheme 7



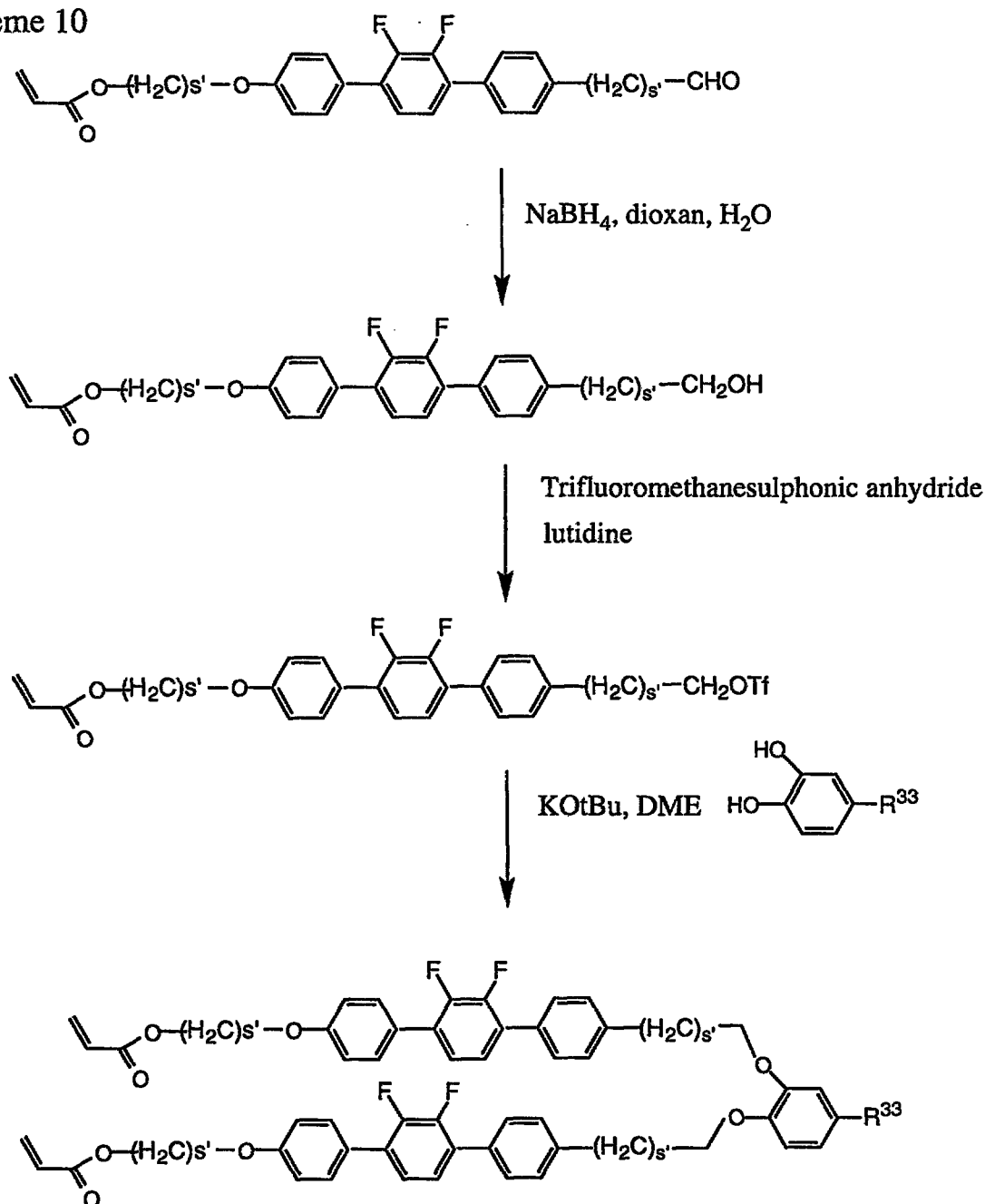
Scheme 8



Scheme 9



Scheme 10



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

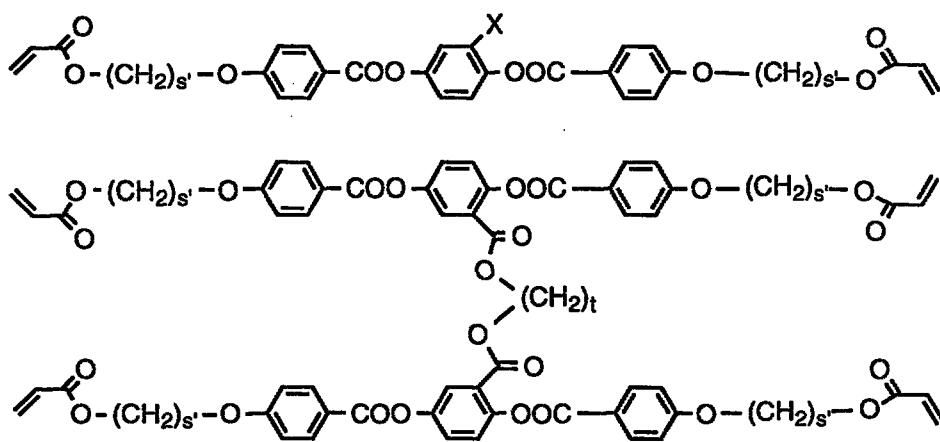
Compounds of formula I in which the cross-linkable side-
 chains are different can be produced by mono-esterifying
 10 2-hydroxyphenols with an (ω-acryloyloxyalkyloxy)-substituted
 carboxylic acid. Subsequent esterification with a different
 (ω-acryloyloxyalkyloxy)-substituted carboxylic acid gives the

asymmetric diester. The corresponding asymmetric diethers are accessible via a similar two-stage process. The starting materials are known and in part are commercially available.

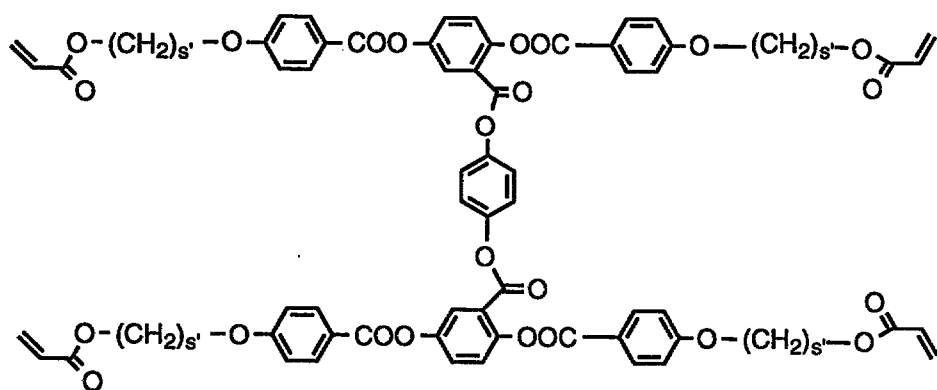
- 5 The compounds of formula I can be used as single compounds or in the form of mixtures with one another and/or with other liquid crystal components.

10 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 optionally additional components can be further compounds of formula I or other known liquid crystalline compounds having a photo cross-linkable group. One or more chiral components can
15 also be present in the mixture.

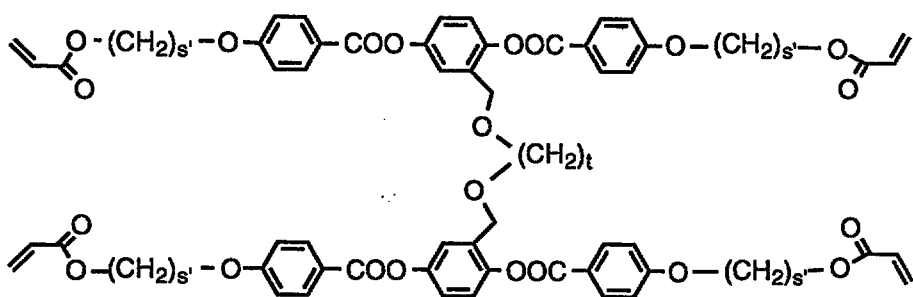
20 Having regard to the good solubility of the compounds of formula I and having regard to their good miscibility with one another, the content of compounds of formula I in the mixtures in accordance with the invention can be high and can amount to 100 wt.%.
25 The mixtures in accordance with the invention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



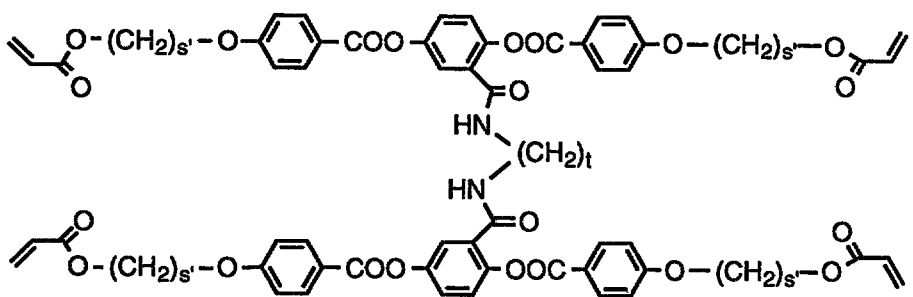
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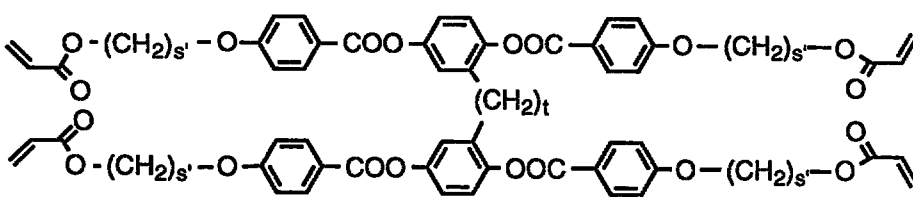
IV



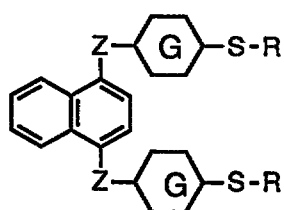
V



VI



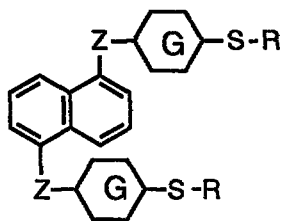
VII



VIII

5

and



IX

wherein

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

15 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.

20

Example 1

0.9 g of triethylamine and then 0.5 g of methanesulphonyl chloride were added dropwise at -25°C while stirring to a
 25 solution of 2.0 g of 4-(4-[8-acryloyloxyoctyloxy]phenylcarbon-yloxy)benzoic acid in 40 ml of tetrahydrofuran. The reaction mixture was stirred at -25°C for 1 hour, treated with 0.28 g of 3,4-dihydroxybenzonitrile and 0.05 g of 4-(dimethylamino)-pyridine, stirred at room temperature overnight, poured into
 30 100 ml of water and then extracted three times with 50 ml of diethyl ether each time. The organic phases were combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate was concentrated.

Chromatographic purification of the 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 were pure according to thin-layer chromatography gave 1.2 g of 3,4-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)phenylcarbonyloxy]benzonitrile; m.p. (C-SA) 70°C, SA-N 139°C, cl.p. (N-I) 152°C.

The 4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzoic acid used as the starting material was prepared as follows:

(a). 3.9 g of N,N'-dicyclohexylcarbodiimide were added at 0°C within 15 minutes while stirring to a solution of 1.9 g of 4-hydroxybenzaldehyde, 5.0 g of 4-[8-acryloyloxyoctyloxy]benzoic acid and 0.1 g of 4-(dimethylamino)pyridine in 100 ml of dichloromethane. The reaction mixture was stirred at room temperature overnight, filtered and the filtrate was concentrated. Chromatographic purification of the residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2) and two-fold recrystallization from ethyl acetate of the fractions which were pure according to thin-layer chromatography gave 5.5 g of 4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzaldehyde; m.p. 73°C.

(b). A solution of 5.5 g of 4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzaldehyde in 100 ml of acetone was treated dropwise with 25 ml of Jones' reagent. The mixture was stirred at room temperature overnight, poured into 100 ml of water and extracted three times with 50 ml of ethyl acetate each time. The organic phases were combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate was concentrated. The residue was recrystallized from ethyl acetate. This gave 3.5 g of 4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzoic acid; m.p. (C-N) 116°C, cl.p. (N-I) 240°C (decomposition).

35

The following compounds can be prepared in an analogous manner:

3,4-bis[4-(4-[3-Acryloyloxypropyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

3,4-bis[4-(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

5 3,4-bis[4-(4-[5-acryloyloxyptyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

10 3,4-bis[4-(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

3,4-bis[4-(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

3,4-bis[4-(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

15 3,4-bis[4-(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

3,4-bis[4-(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzonitrile;

20 1,2-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]benzene; m.p. (C- SA) 89°C, SA-N, 105°C, cl.p. (N-I) 107°C;

methyl 3,4-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)phenylcarbonyloxy]benzoate;

25 ethyl 3,4-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)phenylcarbonyloxy]benzoate; m.p. (C- SA) 25°C, cl.p. (SA-I) 150°C;

3,4-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]toluene;

30 3,4-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1-ethylbenzene;

3,4-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1-propylbenzene.

Example 2

0.9 g of triethylamine and then 0.5 g of methanesulphonyl chloride were added dropwise at -25°C while stirring to a solution of 0.4 g of 3,4-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzoic acid in 40 ml of tetrahydrofuran. The reaction mixture was stirred at -25°C for 1 hour, then treated with 0.06 g of 2-fluoro-4-hydroxybenzonitrile and 0.05 g of 4-(dimethylamino)pyridine in 40 ml of tetrahydrofuran, stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of diethyl ether each time. The organic phases were combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate was concentrated. Chromatographic purification of the residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2) and two-fold recrystallization from ethyl alcohol of the fractions which were pure according to thin-layer chromatography gave 1.2 g of 3,4-bis[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)phenylcarbonyloxy]-2-fluorobenzonitrile; m.p. (C-I) 85°C, cl.p. (N-I) 3°C.

The 3,4-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-benzoic acid used as the starting material was prepared as follows:

(a). 0.6 g of triethylamine and then 0.4 g of methanesulphonyl chloride were added dropwise at -25°C while stirring to a solution of 1.0 g of 4-(8-acryloyloxyoctyloxy)benzoic acid in 40 ml of tetrahydrofuran. The reaction mixture was stirred at -25°C for 1 hour, then treated with 0.20 g of 4-hydroxybenzaldehyde and 0.03 g of 4-(dimethylamino)pyridine in 40 ml of tetrahydrofuran, stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of diethyl ether each time. The organic phases were combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate was concentrated. Chromatographic purification of the 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 were pure according to thin-layer chromatography gave 0.6 g of 3,4-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzaldehyd; m.p. (C-I) 56°C.

- 5 (b). A solution of 0.6 g of 3,4-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzaldehyde in 20 ml of acetone was treated dropwise at 0°C with 2 ml of Jones' reagent. The mixture was stirred at 0°C for 1 hour and then at room temperature overnight, poured into 100 ml of water and filtered, the filter
10 material was washed with water and then dried. This gave 0.4 g of 3,4-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzoic acid.

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

- 3,4-bis[4-(4-[3-Acryloyloxypropyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-2-fluorobenzonitrile;
3,4-bis[4-(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)-
20 phenylcarbonyloxy]-2-fluorobenzonitrile;
3,4-bis[4-(4-[5-acryloyloxypentyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-2-fluorobenzonitrile;
3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-2-fluorobenzonitrile;
25 3,4-bis[4-(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-2-fluorobenzonitrile;
3,4-bis[4-(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-2-fluorobenzonitrile;
3,4-bis[4-(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-
30 phenylcarbonyloxy]-2-fluorobenzonitrile;
3,4-bis[4-(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-2-fluorobenzonitrile;
3,4-bis[4-(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-2-fluorobenzonitrile;
35 3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1-fluorobenzene;

3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1-chlorobenzene;

3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1-bromobenzene;;

5 3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1,2-difluorobenzene;

3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1,2-dichlorobenzene;

10 3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1,2-dicyanobenzene;

3,4-bis[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenylcarbonyloxy]-1-chloro-2-fluorobenzene.

Example 3

15

0.9 g of triethylamine and then 0.5 g of methanesulphonyl chloride are added dropwise at -25°C while stirring to a solution of 2.0 g of 4-(8-acryloyloxyoctyloxy)biphenyl-4'-carboxylic acid in 40 ml of tetrahydrofuran. The reaction mixture is stirred at
20 -25°C for 1 hour, then treated with 0.25 g of 3,4-dihydroxybenzonitrile and 0.05 g of 4-(dimethylamino)pyridine, stirred at room 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
25 100 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 cyclohexane/ethyl acetate mixture (vol. 8:2) of the fractions which are
30 pure according to thin-layer chromatography gives 1.0 g of 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-carbonyloxy]-benzonitrile.

The 4-(8-acryloyloxyoctyloxy)biphenyl-4'-carboxylic acid
35 used as the starting material is prepared as follows:

(a). A solution of 5.0 g of 4'-hydroxybiphenyl-4-carbonitrile and 5.1 g of 8-chloro-1-octanol in 100 ml of ethyl methyl ketone is treated with 14.1 g of finely powdered potassium carbonate and the mixture is heated under slight reflux overnight.

5 The suspension is suction filtered and the filtrate is concentrated in a vacuum. Chromatography of the residue on silica gel with hexane/ethyl acetate (vol. 1:1) gives 4.9 g of 4'-(8-hydroxyoctyloxy)biphenyl-4-carbonitrile.

10 (b). A solution of 4.9 g of 4-cyano-4'-(8-hydroxyoctyloxy)biphenyl in 25 ml of toluene is treated at 0°C with 50 ml of a 1.2M solution of diisobutylaluminium hydride in toluene and the mixture is stirred at room temperature overnight. The reaction mixture is poured into 100 ml of 1.0N sulphuric acid and
15 extracted twice with 50 ml of ethyl acetate each time. The organic phases are washed with 50 ml of water, dried over magnesium sulphate and concentrated. Chromatography of the residue on silica gel with hexane/ethyl acetate (vol. 8:2) and recrystallization from ethyl alcohol of the fractions which are
20 pure according to thin-layer chromatography gives 3.8 g of 4-formyl-4'-(8-hydroxyoctyloxy)biphenyl.

(c). 2.9 g of N,N'-dicyclohexylcarbodiimide are added within 5 minutes while stirring to a solution of 3.8 g of
25 4-formyl-4'-(8-hydroxyoctyloxy)biphenyl, 0.9 g of acrylic acid and 0.05 g of 4-(dimethylamino)pyridine in 25 ml of dichloromethane. The reaction mixture is stirred overnight, filtered and then concentrated. Chromatography of the residue on silica gel with hexane/ethyl acetate (vol. 8:2) and recrystallization from
30 ethyl alcohol of the fractions which are pure according to thin-layer chromatography gives 2.5 g of 4-formyl-4'-(8-acryloyloxyoctyloxy)biphenyl.

(d). A solution of 2.5 g of 4-formyl-4'-(8-acryloyloxyoctyloxy)biphenyl in 100 ml of acetone is treated dropwise with
35 10 ml of Jones' reagent. The mixture is stirred at room temperature for 1 hour and then at room temperature overnight, poured into 100 ml of water and then extracted three times with

50 ml of ethyl acetate each time. The combined organic phases are washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate is concentrated. The residue is recrystallized from ethyl acetate. This gives
 5 1.6 g of 4-(8-acryloyloxyoctyloxy)biphenyl-4'-carboxylic acid.

The following compounds can be prepared in an analogous manner:

10 3,4-bis[4-(3-Acryloyloxypropyloxy)biphenyl-4'-carbonyloxy]-benzonitrile;

3,4-bis[4-(4-acryloyloxybutyloxy)biphenyl-4'-carbonyloxy]-benzonitrile;

15 3,4-bis[4-(5-acryloyloxypentyloxy)biphenyl-4'-carbonyloxy]-benzonitrile;

3,4-bis[4-(6-acryloyloxyhexyloxy)biphenyl-4'-carbonyloxy]-benzonitrile;

3,4-bis[4-(7-acryloyloxyheptyloxy)biphenyl-4'-carbonyloxy]-benzonitrile;

20 3,4-bis[4-(9-acryloyloxynonyloxy)biphenyl-4'-carbonyloxy]-benzonitrile;

3,4-bis[4-(10-acryloyloxydecyloxy)biphenyl-4'-carbonyloxy]-benzonitrile;

25 3,4-bis[4-(11-acryloyloxyundecyloxy)biphenyl-4'-carbonyloxy]benzonitrile;

3,4-bis[4-(12-acryloyloxydodecyloxy)biphenyl-4'-carbonyloxy]benzonitrile;

methyl 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-carbonyloxy]benzoate;

30 ethyl 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-carbonyloxy]benzoate;

propyl 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-carbonyloxy]benzoate;

35 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-carbonyloxy]toluene;

3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-carbonyloxy]-1-ethylbenzene;

3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-carbonyloxy]-1-propylbenzene;

5

Example 4

0.9 g of triethylamine and then 0.5 g of methanesulphonyl chloride are added dropwise at -25°C while stirring to a solution of 2.0 g of 4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)benzoic
 10 acid in 40 ml of tetrahydrofuran. The reaction mixture is stirred at -25°C for 1 hour, then treated with 0.28 g of 3,4-dihydroxybenzonitrile and 0.05 g of 4-(dimethylamino)pyridine, stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of diethyl ether each
 15 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 cyclo-
 20 hexane/ethyl acetate mixture (vol. 8:2) of the fractions which are pure according to thin-layer chromatography gives 1.1 g of 3,4-bis[4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)phenylcarbonyloxy]benzonitrile.

25 The 4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)benzoic acid used as the starting material is prepared as follows:

(a). A mixture of 10.0 g of 4-(5-benzyloxypyrimidin-2-yl)benzaldehyde, 0.2 g of sodium carbonate and 250 ml of ethyl
 30 acetate is treated with 1.0 g of palladium on active charcoal (10%) and hydrogenated at normal pressure and room temperature until the hydrogen uptake comes to a standstill. The inorganic material is filtered off over Sillit and the filtrate is concentrated. Recrystallization of the crude product from hexane gives
 35 6.1 g of pure 4-(5-hydroxypyrimidin-2-yl)benzaldehyde.

(b). A solution of 6.1 g of 4-(5-hydroxypyrimidin-2-yl)benzaldehyde and 6.0 g of 8-chloro-1-octanol in 100 ml of

ethyl methyl ketone is treated with 16.9 g of finely powdered potassium carbonate and the mixture is heated under slight reflux overnight. The suspension is suction filtered and the filtrate is concentrated in a vacuum. Chromatography of the residue on
 5 silica gel with hexane/ethyl acetate (vol. 1:1) gives 5.5 g of 4-(5-[8-hydroxyoctyloxy]pyrimidin-2-yl)benzaldehyde.

(c). 4.2 g of N,N'-dicyclohexylcarbodiimide are added within 5 minutes while stirring to a solution of 5.5 g of 4-(5-[8-
 10 hydroxyoctyloxy]pyrimidin-2-yl)benzaldehyde, 1.2 g of acrylic acid and 0.2 g of 4-(dimethylamino)pyridine in 25 ml of dichloromethane. The reaction mixture is stirred overnight, filtered and the filtrate is concentrated. Chromatography of the residue on silica gel with hexane/ethyl acetate (vol. 8:2) and
 15 recrystallization from ethyl alcohol of the fractions which are pure according to thin-layer chromatography gives 4.8 g of 4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)benzaldehyde.

(d). A solution of 3.2 g of 4-(5-[8-acryloyloxyoctyloxy]-
 20 pyrimidin-2-yl)benzaldehyde in 100 ml of acetone is treated dropwise with 20 ml of Jones' reagent. The mixture is stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of ethyl acetate each time. The organic phases are combined, washed twice with
 25 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate is concentrated. The residue is recrystallized from ethyl acetate. This gives 2.0 g of 4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)benzoic acid.

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

3,4-bis[4-(5-[3-acryloyloxypropyloxy]pyrimidin-2-yl)phenyl-carbonyloxy]benzonitrile;

35 3,4-bis[4-(5-[4-acryloyloxybutyloxy]pyrimidin-2-yl)phenyl-carbonyloxy]benzonitrile;

3,4-bis[4-(5-[5-acryloyloxypentyloxy]pyrimidin-2-yl)phenyl-carbonyloxy]benzonitrile;

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

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

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

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

10 3,4-bis[4-(5-[11-acryloyloxyundecyloxy]pyrimidin-2-yl)-phenylcarbonyloxy]benzonitrile;

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

methyl 3,4-bis[4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)-phenylcarbonyloxy]benzoate;

15 ethyl 3,4-bis[4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)-phenylcarbonyloxy]benzoate;

propyl 3,4-bis[4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)-phenylcarbonyloxy]benzoate;

20 3,4-bis[4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)-phenylcarbonyloxy]toluene;

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

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

25 3,4-bis[2-(4-[3-acryloyloxypropyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

3,4-bis[2-(4-[4-acryloyloxybutyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

30 3,4-bis[2-(4-[5-acryloyloxypentyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

3,4-bis[2-(4-[6-acryloyloxyhexyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

3,4-bis[2-(4-[7-acryloyloxyheptyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

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

3,4-bis[2-(4-[9-acryloyloxynonyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

5 3,4-bis[2-(4-[10-acryloyloxydecyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

3,4-bis[2-(4-[11-acryloyloxyundecyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

10 3,4-bis[2-(4-[12-acryloyloxydodecyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzonitrile;

 methyl 3,4-bis[2-(4-[3-acryloyloxypropyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzoate;

 ethyl 3,4-bis[2-(4-[3-acryloyloxypropyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzoate;

15 propyl 3,4-bis[2-(4-[3-acryloyloxypropyloxy]phenyl)pyridin-5-ylcarbonyloxy]benzoate;

 3,4-bis[2-(4-[3-acryloyloxypropyloxy]phenyl)pyridin-5-ylcarbonyloxy]toluene;

 3,4-bis[2-(4-[3-acryloyloxypropyloxy]phenyl)pyridin-5-ylcarbonyloxy]-1-ethylbenzene;

20 3,4-bis[2-(4-[3-acryloyloxypropyloxy]phenyl)pyridin-5-ylcarbonyloxy]-1-propylbenzene.

Example 5

25

 A solution of 1.1 g of 4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)benzyl alcohol, 0.2 g of 3,4-dihydroxybenzonitrile, 0.5 g of diethyl azodicarboxylate, 0.7 g of triphenylphosphine and 50 ml of tetrahydrofuran is stirred overnight and then concentrated. The residue is suspended in 50 ml of hot hexane and filtered. 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 cyclohexane/ethyl acetate mixture (vol. 8:2) of the fractions which are pure according to thin-layer chromatography gives 1.2 g of 3,4-bis([4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)phenyl]methoxy)benzonitrile.

The 4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)benzyl alcohol used as the starting material is prepared as follows:

A mixture of 0.3 g of sodium borohydride and 30 ml of water
 5 is treated dropwise at 0°C with a solution of 1.6 g of 4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)benzyl aldehyde in 100 ml of dioxan. The reaction mixture is stirred at 0°C for 60 minutes and then at room temperature for 10 minutes, poured into 100 ml of dichloromethane and washed twice with 100 ml of water each
 10 time. The aqueous phases are combined and extracted twice with 50 ml of dichloromethane each time. The organic phases are combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, the suspension is filtered and the filtrate is concentrated. This gives 1:1 g of 4-(5-[8-acryloyl-
 15 oxyoctyloxy]pyrimidin-2-yl)benzyl alcohol.

The following compounds can be prepared in an analogous manner:

20 3,4-bis([4-(5-[3-Acryloyloxypropyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

3,4-bis([4-(5-[4-acryloyloxybutoxy]pyrimidin-2-yl)phenyl]-methoxy)benzonitrile;

25 3,4-bis([4-(5-[5-acryloyloxyptyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

3,4-bis([4-(5-[6-acryloyloxyhexyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

3,4-bis([4-(5-[7-acryloyloxyheptyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

30 3,4-bis([4-(5-[8-acryloyloxyoctyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

3,4-bis([4-(5-[9-acryloyloxynonyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

35 3,4-bis([4-(5-[10-acryloyloxydecyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

3,4-bis([4-(5-[11-acryloyloxyundecyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

3,4-bis([4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)-phenyl]methoxy)benzonitrile;

5 methyl 3,4-bis([4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)phenyl]methoxy)benzoate;

ethyl 3,4-bis([4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)phenyl]methoxy)benzoate;

10 propyl 3,4-bis([4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)phenyl]methoxy)benzoate;

3,4-bis([4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)-phenyl]methoxy)toluene;

3,4-bis([4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)-phenyl]methoxy)-1-ethylbenzene;

15 3,4-bis([4-(5-[12-acryloyloxydodecyloxy]pyrimidin-2-yl)-phenyl]methoxy)-1-propylbenzene;

3,4-bis([4-(5-[8-acryloyloxyoctyloxy]pyridin-2-yl)phenyl]-methoxy)benzonitrile;

20 3,4-bis([2-(4-[3-acryloyloxypropyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

3,4-bis([2-(4-[4-acryloyloxybutyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

3,4-bis([2-(4-[5-acryloyloxypropyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

25 3,4-bis([2-(4-[6-acryloyloxyhexyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

3,4-bis([2-(4-[7-acryloyloxyheptyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

30 3,4-bis([2-(4-[8-acryloyloxyoctyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

3,4-bis([2-(4-[9-acryloyloxydecyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

3,4-bis([2-(4-[10-acryloyloxyundecyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

3,4-bis([2-(4-[11-acryloyloxyundecyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

3,4-bis([2-(4-[12-acryloyloxydodecyloxy]phenyl)pyridin-5-yl]methoxy)benzonitrile;

5 methyl 3,4-bis([2-(4-[8-acryloyloxyoctyloxy]phenyl)pyridin-5-yl]methoxy)benzoate;

ethyl 3,4-bis([2-(4-[8-acryloyloxyoctyloxy]phenyl)pyridin-5-yl]methoxy)benzoate;

10 propyl 3,4-bis([2-(4-[8-acryloyloxyoctyloxy]phenyl)pyridin-5-yl]methoxy)benzoate;

3,4-bis([2-(4-[8-acryloyloxyoctyloxy]phenyl)pyridin-5-yl]-methoxy)toluene;

3,4-bis([2-(4-[8-acryloyloxyoctyloxy]phenyl)pyridin-5-yl]-methoxy)-1-ethylbenzene;

15 3,4-bis([2-(4-[8-acryloyloxyoctyloxy]phenyl)pyridin-5-yl]-methoxy)-1-propylbenzene;

3,4-bis[4-(3-acryloyloxypropyloxy)biphenyl-4'-methoxy]-benzonitrile;

20 3,4-bis[4-(4-acryloyloxybutyloxy)biphenyl-4'-methoxy]-benzonitrile;

3,4-bis[4-(5-acryloyloxypropyloxy)biphenyl-4'-methoxy]-benzonitrile;

3,4-bis[4-(6-acryloyloxyhexyloxy)biphenyl-4'-methoxy]-benzonitrile;

25 3,4-bis[4-(7-acryloyloxyheptyloxy)biphenyl-4'-methoxy]-benzonitrile;

3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-methoxy]-benzonitrile;

30 3,4-bis[4-(9-acryloyloxynonyloxy)biphenyl-4'-methoxy]-benzonitrile;

3,4-bis[4-(10-acryloyloxydecyloxy)biphenyl-4'-methoxy]-benzonitrile;

3,4-bis[4-(11-acryloyloxyundecyloxy)biphenyl-4'-methoxy]-benzonitrile;

3,4-bis[4-(12-acryloyloxydodecyloxy)biphenyl-4'-methoxy]-benzonitrile;

methyl 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-methoxy]benzoate;

5 ethyl 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-methoxy]benzoate;

propyl 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-methoxy]benzoate;

10 3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-methoxy]-toluene;

3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-methoxy]-1-ethylbenzene;

3,4-bis[4-(8-acryloyloxyoctyloxy)biphenyl-4'-methoxy]-1-propylbenzene;

15

Example 6

0.9 g of triethylamine and then 0.5 g of methanesulphonyl chloride are added dropwise at -25°C while stirring to a solution of 2.0 g of trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-
 20 cyclohexanecarboxylic acid and 40 ml of tetrahydrofuran. The reaction mixture is stirred at -25°C for 1 hour, then treated with 0.28 g of 3,4-dihydroxybenzonitrile and 0.05 g of 4-(dimethyl-amino)pyridine, stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml
 25 of diethyl ether each time. The combined organic phases are 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 cyclohexane/ethyl acetate (vol. 8:2) and two-fold recrystal-
 30 lization 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 3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)cyclohexanecarbonyloxy]benzonitrile.

The trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-cyclohexanecarboxylic acid used as the starting material is prepared as follows:

- 5 (a). A solution of 0.3 ml of 35% hydrochloric acid and 10.0 g of methyl trans-4-(trans-4-[2-(1,3-dioxan-2-yl)ethyl]-cyclohexyl)cyclohexanecarboxylate in 100 ml of toluene is stirred at room temperature overnight and poured into 100 ml of water. The organic phase is separated, washed twice with 100 ml of
10 water each time, dried over magnesium sulphate, the suspension is filtered and the filtrate is concentrated. This gives 7.4 g of methyl trans-4-(trans-4-[2-formylethyl]cyclohexyl)cyclohexanecarboxylate.
- 15 (b). A mixture of 1.4 g of sodium borohydride and 140 ml of water is treated dropwise at 0°C with a solution of 7.4 g of methyl trans-4-(trans-4-[2-formylethyl]cyclohexyl)cyclohexanecarboxylate in 100 ml of dioxan. The reaction mixture is stirred at 0°C for 60 minutes and then at room temperature for
20 10 minutes, poured into 100 ml of dichloromethane and washed twice with 100 ml of water each time. The aqueous phases are combined, extracted twice with 50 ml of dichloromethane each time. The organic phases are combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, the
25 suspension is filtered and the filtrate is concentrated. This gives 6.3 g of methyl trans-4-(trans-4-[3-hydroxypropyl]cyclohexyl)cyclohexanecarboxylate.
- 30 (c). A solution of 2.0 g of potassium hydroxide, 20 ml of water and 6.3 g of methyl trans-4-(trans-4-[3-hydroxypropyl]cyclohexyl)cyclohexanecarboxylate in 100 ml of ethyl alcohol is heated under slight reflux for 2 hours, poured into 100 ml of water and acidified with 25% hydrochloric acid. The precipitate is filtered off, washed portionwise with water and
35 dried. This gives 5.2 g of trans-4-(trans-4-[3-hydroxypropyl]cyclohexyl)cyclohexanecarboxylic acid.

(d). 4.2 g of N,N'-dicyclohexylcarbodiimide are added within 5 minutes while stirring to a solution of 5.2 g of trans-4-(trans-4-[3-hydroxypropyl]cyclohexyl)cyclohexanecarboxylic acid, 1.2 g of acrylic acid and 0.2 g 4-(dimethylamino)pyridine in 5 25 ml of dichloromethane. The reaction mixture is stirred overnight, filtered and then concentrated. Chromatography of the residue on silica gel with hexane/ethyl acetate (vol. 8:2) and recrystallization from ethyl alcohol of the fractions which are pure according to thin-layer chromatography gives 4.2 g of 10 trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)cyclohexanecarboxylic acid.

The following compounds can be prepared in an analogous manner:

15

3,4-bis[trans-4-(trans-4-[3-Acryloyloxypropyl]cyclohexyl)-cyclohexanecarbonyloxy]-2-fluorobenzonitrile;

3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-cyclohexanecarbonyloxy]-1-fluorobenzene;

20

3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-cyclohexanecarbonyloxy]-1-chlorobenzene;

3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-cyclohexanecarbonyloxy]-1-bromobenzene;

25

3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-cyclohexanecarbonyloxy]toluene;

3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-cyclohexanecarbonyloxy]-1-ethylbenzene;

3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-cyclohexanecarbonyloxy]-1-propylbenzene;

30

methyl 3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)cyclohexanecarbonyloxy]benzoate;

ethyl 3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)cyclohexanecarbonyloxy]benzoate;

propyl 3,4-bis[trans-4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)cyclohexanecarbonyloxy]benzoate;

35

3,4-bis[trans-4-(2-[trans-4-(3-acryloyloxypropyl)cyclohexyl]ethyl)cyclohexanecarbonyloxy]benzonitrile;

methyl 3,4-bis[trans-4-(2-[trans-4-(3-acryloyloxypropyl)-cyclohexyl]ethyl)cyclohexanecarbonyloxy]benzoate;

5 ethyl 3,4-bis[trans-4-(2-[trans-4-(3-acryloyloxypropyl)-cyclohexyl]ethyl)cyclohexanecarbonyloxy]benzoate;

3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)phenyl-carbonyloxy]benzonitrile;

3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)phenyl-carbonyloxy]-2-fluorobenzonitrile;

3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)phenyl-carbonyloxy]-1-fluorobenzene;

3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)phenyl-carbonyloxy]-1-chlorobenzene;

15 3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)phenyl-carbonyloxy]-1-bromobenzene;

3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)phenyl-carbonyloxy]toluene;

3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)phenyl-carbonyloxy]-1-ethylbenzene;

3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)phenyl-carbonyloxy]-1-propylbenzene;

methyl 3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-phenylcarbonyloxy]benzoate;

25 ethyl 3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-phenylcarbonyloxy]benzoate;

propyl 3,4-bis[4-(trans-4-[3-acryloyloxypropyl]cyclohexyl)-phenylcarbonyloxy]benzoate;

3,4-bis[4-(2-[trans-4-(3-acryloyloxypropyl)cyclohexyl]-ethyl)phenylcarbonyloxy]benzonitrile;

methyl 3,4-bis[4-(2-[trans-4-(3-acryloyloxypropyl)cyclohexyl]ethyl)phenylcarbonyloxy]benzoate;

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

Example 7

A solution of 0.433 g of N-ethyl-N'-(3-dimethylamino-propyl)-carbodiimide hydrochloride (EDC) in 5 ml of dichloromethane is slowly added dropwise at 0°C to a solution of 1.00 g of 6-[4'-[trans-4-(2-carboxy-ethyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate, 0.127 g of 3,4-dihydroxybenzonitrile and 0.255 g of 4-dimethylamino-pyridine (DMAP) in 30 ml of dichloromethane, the mixture is stirred at room temperature overnight, poured into 50 ml of water and then extracted three times with 25 ml of diethyl ether each time. The combined organic phases are washed twice with 50 ml of water each time, dried over magnesium sulphate, filtered and subsequently concentrated. Chromatographic purification of the 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 0.48 g of 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzonitrile.

The 6-[4'-[trans-4-(2-carboxy-ethyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate used as the starting material is prepared as follows:

25

(a). A solution of 5.238 g of dihydroxy-[4-(6-hydroxy-hexyloxy)-phenyl]-borane, 8.206 g of 4-[trans-4-(2-[1,3]dioxolan-2-yl-ethyl)-cyclohexyl]-phenyl trifluoromethanesulphonate, 6.368 g of tripotassium phosphate, 2.619 g of potassium bromide and 0.578 g of tetrakis-(triphenylphosphine)-palladium in 100 ml of dioxan is stirred overnight at 85°C under nitrogen. After cooling the solution is diluted with 100 ml of ether, washed three times with 50 ml of water each time, dried over magnesium sulphate, filtered and concentrated. The residue is purified by column chromatography on silica gel with cyclohexane/ethyl acetate (vol. 8:2). This gives 6.2 g of 6-[4'-[trans-4-(2-[1,3]dioxolan-2-yl-ethyl)cyclohexyl]-biphenyl-4-yloxy]-hexan-1-ol.

(b). 3.38 g of dicyclohexylcarbodiimide in 5 ml of dichloromethane is added dropwise while stirring at 0-5°C within 5 minutes to a solution of 6.2 g of 6-[4'-[trans-4-(2-[1,3]-dioxolan-2-yl-ethyl)cyclohexyl]-biphenyl-4-yloxy]-hexan-1-ol, 1.48 g of acrylic acid and 1.67 g of 4-dimethylamino-pyridine in 50 ml of dichloromethane. The reaction mixture is stirred overnight, filtered and then concentrated. Chromatography of the residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2) gives 5.14 g of 6-[4'-[trans-4-(2-[1,3]dioxolan-2-yl-ethyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate.

(c). 5.14 g of 6-[4'-[trans-4-(2-[1,3]dioxolan-2-yl-ethyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate are dissolved in 100 ml of toluene. After the addition of 50 ml of formic acid the mixture is stirred at room temperature for 4 hours. Then, the organic phase is separated and the aqueous phase is extracted twice with 50 ml of toluene. The combined organic phases are washed twice with 100 ml of water, dried over magnesium sulphate and concentrated. This gives 4.55 g of 6-[4'-[trans-4-(3-oxo-propyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate.

(d). A solution of 4.55 g of 6-[4'-[trans-4-(3-oxo-propyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate in 100 ml of acetone is treated dropwise at 5°C with 20 ml of Jones' reagent. The mixture is stirred at room temperature overnight, poured into 100 ml of water and extracted three times with 50 ml of ethyl acetate. The organic phases are combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and concentrated. This gives 3.86 g of 6-[4'-[trans-4-(2-carboxy-ethyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate.

The following compounds can be prepared in an analogous manner:

3,4-Bis-[3-[trans-4-[4'-(3-acryloyloxy-propyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzonitrile;

- 3,4-bis-[3-[trans-4-[4'-(4-acryloyloxy-butyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzonitrile;
 3,4-bis-[3-[trans-4-[4'-(5-acryloyloxy-pentyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzonitrile;
 5 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzonitrile;
 methyl 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzoate;
 ethyl 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-
 10 biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzoate;
 propyl 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzoate;
 octyl 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzoate;
 15 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-benzene;
 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-toluene;
 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-
 20 4-yl]-cyclohexyl]-propionyloxy]-ethylbenzene;
 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propionyloxy]-propylbenzene.

Example 8

25

A solution of 1.50 g of 6-[4'-[trans-4-[3-(trifluoromethanesulphonyl)-propyl]-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate and 0.155 g of 3,4-dihydroxy-benzonitrile in 25 ml of 1,2-dimethoxyethane is treated portionwise at 0°C with 0.286 g
 30 of potassium tertiary butylate and subsequently stirred overnight at 85°C. The cooled reaction mixture is poured into 25 ml of water and then extracted three times with 20 ml of ethyl acetate. The combined organic phases are washed twice with 50 ml of water, dried over magnesium sulphate, filtered and
 35 concentrated. Chromatographic purification of the 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 1.10 g of 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]-benzonitrile.

- 5 The 6-[4'-[trans-4-[3-(trifluoromethanesulphonyl)-propyl]-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate used as the starting material is prepared as follows:

(a). A mixture of 0.123 g of sodium borohydride and 10 ml
10 of water is treated dropwise at 0°C with a solution of 5.00 g of 6-[4'-[trans-4-(3-oxo-propyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate in 50 ml of dioxan. The mixture is subsequently stirred at room temperature for 1 hour. The reaction mixture is poured into 50 ml of water, the phases are separated and the
15 aqueous phase is extracted twice with 25 ml of ethyl acetate each time. The combined organic phases are washed twice with 50 ml of water each time, dried over magnesium sulphate, filtered and concentrated. Chromatographic purification of the residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2)
20 gives 4.77 g of 6-[4'-[trans-4-(3-hydroxy-propyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate.

(b). 3.47 g of trifluoromethanesulphonic anhydride dissolved in 10 ml of dichloromethane are added dropwise at 0°C
25 to a solution of 4.77 g of 6-[4'-[trans-4-(3-hydroxy-propyl)-cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate and 1.32 g of lutidine in 100 ml of dichloromethane. The reaction mixture is stirred at 0°C for 90 minutes and subsequently poured into 100 ml of water and extracted twice with 50 ml of dichloro-
30 methane. The combined organic phases are washed twice with 50 ml of water each time, dried over magnesium sulphate and concentrated. Chromatographic purification of the residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2) gives 5.09 g of [4'-[trans-4-[3-(trifluoromethanesulphonyloxy)-propyl]-
35 cyclohexyl]-biphenyl-4-yloxy]-hexyl acrylate.

The following compounds can be prepared in an analogous manner:

- 3,4-Bis-[3-[trans-4-[4'-(3-acryloyloxy-propyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzonitrile;
- 3,4-bis-[3-[trans-4-[4'-(4-acryloyloxy-butyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzonitrile;
- 3,4-bis-[3-[trans-4-[4'-(5-acryloyloxy-pentyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzonitrile;
- 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzonitrile;
- 10 methyl 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzoate;
- ethyl 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzoate;
- propyl 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzoate;
- 15 octyl 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzoate;
- 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]benzene;
- 20 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]toluene;
- 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]ethylbenzene;
- 3,4-bis-[3-[trans-4-[4'-(6-acryloyloxy-hexyloxy)-biphenyl-4-yl]-cyclohexyl]-propoxy]propylbenzene.
- 25

Example 9

A solution of 0.418 g of N-ethyl-N'-(3-dimethylamino-propyl)-carbodiimide hydrochloride (EDC) in 5 ml of dichloromethane is slowly added dropwise at 0°C to a solution of 1.00 g of 4-[2',3'-difluoro-4''-(3-carboxy-propyl)-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate, 0.123 g of 3,4-dihydroxybenzonitrile and 0.247 g of 4-dimethylamino-pyridine (DMAP) in 30 ml of

35 dichloromethane, the mixture is stirred at room temperature overnight, poured into 50 ml of water and then extracted three times with 25 ml of diethyl ether each time. The combined organic phases are washed twice with 50 ml of water each time,

dried over magnesium sulphate, filtered and subsequently concentrated. Chromatographic purification of the 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 0.39 g of 3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzonitrile.

- 10 The 4-[2',3'-difluoro-4''-(3-carboxy-propyl)-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate used as the starting material is prepared as follows:

(a). 13.0 ml of a 1.6 molar solution of butyllithium in
 15 hexane is slowly added dropwise to a solution of 5.80 g of 2-[3-(2',3'-difluoro-biphenyl-4-yl)-propyl]-[1,3]dioxolane in 80 ml of dry tetrahydrofuran under nitrogen at -78°C and the mixture is stirred at this temperature for 2.5 hours. Then, a solution of 4.32 g of trimethyl borate in 10 ml of tetrahydrofuran is added
 20 dropwise thereto. The solution is left to warm slowly and is stirred at room temperature overnight. Then, 50 ml of 10% hydrochloric acid are added thereto, the mixture is stirred for one hour, the phases are separated and extracted twice with 25 ml of ether. The combined organic phases are washed twice with
 25 50 ml of water, dried over magnesium sulphate, filtered and concentrated. This gives 5.3 g of [2,3-difluoro-4'-(4-oxo-butyl)-biphenyl-4-yl]-dihydroxy-borane.

(b). A solution of 5.30 g of [2,3-difluoro-4'-(4-oxo-butyl)-
 30 biphenyl-4-yl]-dihydroxy-borane, 6.18 g of 3-(bromo-phenoxy)-propyl acrylate, 0.50 g of tetrakis-(triphenylphosphine)-palladium and 17.5 ml of 2M sodium carbonate solution in 100 ml of 1,2-dimethoxyethane is stirred overnight at 85°C under nitrogen. After cooling the solution is diluted with 100 ml of
 35 ether, washed three times with 50 ml of water each time, dried over magnesium sulphate, filtered and concentrated. The residue is purified by column chromatography on silica gel with cyclohexane/ethyl acetate (vol. 8:2). This gives 5.55 g of 4-[2',3'-

difluoro-4''-(4-oxo-butyl)-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate.

(c). A solution of 5.55 g of 4-[2',3'-difluoro-4''-(4-oxo-butyl)-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate in 100 ml of acetone is treated dropwise at 5°C with 20 ml of Jones' reagent. The mixture is stirred at room temperature overnight, poured into 100 ml of water and extracted three times with 50 ml of ethyl acetate. The organic phases are combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and concentrated. This gives 5.29 g of 4-[2',3'-difluoro-4''-(3-carboxy-propyl)-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate.

The following compounds can be prepared in an analogous manner:

3,4-Bis-[4-[4''-(3-acryloyloxy-propoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzonitrile;
 3,4-bis-[4-[4''-(5-acryloyloxy-pentoxo)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzonitrile;
 3,4-bis-[4-[4''-(6-acryloyloxy-hexoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzonitrile;
 methyl 3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzoate;
 ethyl 3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzoate;
 propyl 3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzoate;
 octyl 3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzoate;
 3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-benzene;
 3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-toluene;
 3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-ethylbenzene;

3,4-bis-[4-[4''-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butyryloxy]-propylbenzene.

Example 10

5

A solution of 1.50 g of 4-[2',3'-difluoro-4''-[4-(trifluoromethanesulphonyloxy)-butyl]-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate and 0.156 g of 3,4-dihydroxybenzonitrile in 25 ml of 1,2-dimethoxyethane is treated portionwise at 0°C with 0.292 g
 10 of potassium tertiary butylate and the mixture is subsequently stirred at 85°C overnight. The cooled reaction mixture is poured into 25 ml of water and then extracted three times with 20 ml of ethyl acetate. The combined organic phases are washed twice with 50 ml of water, dried over magnesium sulphate, filtered and
 15 concentrated. Chromatographic purification of the 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 0.65 g of 3,4-bis-[4-[4-(4-acryloyloxy-
 20 butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzonitrile.

The 4-[2',3'-difluoro-4''-[4-(trifluoromethanesulphonyloxy)-butyl]-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate used as the starting material is prepared as follows:

25

(a). A mixture of 0.119 g of sodium borohydride and 10 ml of water is treated dropwise at 0°C with a solution of 5.00 g of 4-[2',3'-difluoro-4''-(4-oxo-butyl)-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate in 50 ml of dioxan. The mixture is subsequently
 30 stirred at room temperature for 1 hour. The reaction mixture is poured into 50 ml of water, the phases are separated and the aqueous phase is extracted twice with 25 ml of ethyl acetate each time. The combined organic phases are washed twice with 50 ml of water each time, dried over magnesium sulphate,
 35 filtered and concentrated. Chromatographic purification of the residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2) gives 4.49 g of 4-[2',3'-difluoro-4''-(4-hydroxy-butyl)-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate.

(b). 3.10 g of trifluoromethanesulphonic anhydride dissolved in 10 ml of dichloromethane is added dropwise at 0°C to a solution of 4.40 g of 4-[2',3'-difluoro-4''-(4-hydroxy-butyl)-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate and 1.18 g of lutidine in 100 ml of dichloromethane. The reaction mixture is stirred at 0°C for 90 minutes and subsequently poured into 100 ml of water and extracted twice with 50 ml of dichloromethane. The combined organic phases are washed twice with 50 ml of water each time, dried over magnesium sulphate and concentrated. Chromatographic purification of the residue on silica gel with cyclohexane/ethyl acetate (vol. 8:2) gives 4.20 g of 4-[2',3'-difluoro-4''-[4-(trifluoro-methanesulphonyloxy)-butyl]-1,2':4',1''-terphenyl-4-yloxy]-butyl acrylate.

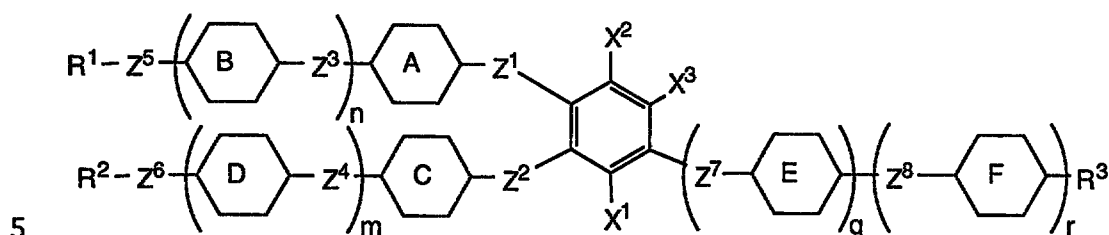
The following compounds can be prepared in an analogous manner:

- 3,4-Bis-[4-[4-(3-acryloyloxy-propoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzonitrile;
- 3,4-bis-[4-[4-(5-acryloyloxy-pentoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzonitrile;
- 3,4-bis-[4-[4-(6-acryloyloxy-hexoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzonitrile;
- methyl 3,4-bis-[4-[4-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzoate;
- ethyl 3,4-bis-[4-[4-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzoate;
- propyl 3,4-bis-[4-[4-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzoate;
- octyl 3,4-bis-[4-[4-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzoate;
- 3,4-bis-[4-[4-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]benzene;
- 3,4-bis-[4-[4-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]ethylbenzene;
- 3,4-bis-[4-[4-(4-acryloyloxy-butoxy)-2',3'-difluoro-1,1':4',1''-terphenyl]-butoxy]propylbenzene.



Claims

1. Compounds of the general formula



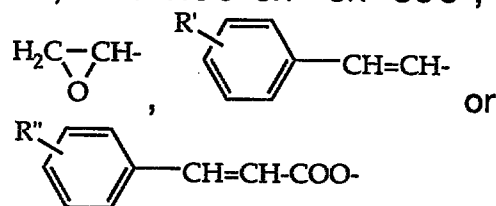
I

wherein

- 10 rings A - F each signify pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or independently of one another 1,4-phenylene optionally substituted with halogen, methyl and/or cyano;
- 15 Z¹, Z² and Z⁷ independently of one another signify -CH₂-(CH₂)_s-, -(CH₂)_sO-, -O(CH₂)_s-, -COO-, -OOC-, -(CH₂)_sCOO- or -(CH₂)_sOOC-;
- 20 Z³, Z⁴ and Z⁸ independently of one another signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;
- 25 Z⁵ and Z⁶ signify -(CY₂)_s-, -O(CY₂)_s-, -(CY₂)_sO-, -(CY₂)_sCOO-, -(CY₂)_sOOC-, -(Si[(CH₃)₂]O)_s-, -OCH₂(Si[(CH₃)₂]O)_sSi[(CH₃)₂]CH₂O-, or -NHCH₂(Si[(CH₃)₂]O)_sSi[(CH₃)₂]CH₂NH-;
- 30 Y signifies hydrogen or fluorine;
- 35 m, n, q and r independently of one another signify 0, 1 or 2;
- 30 s signifies a whole number of 1 to 16;
- 35 R¹ and R² signify cross-linkable groups 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'

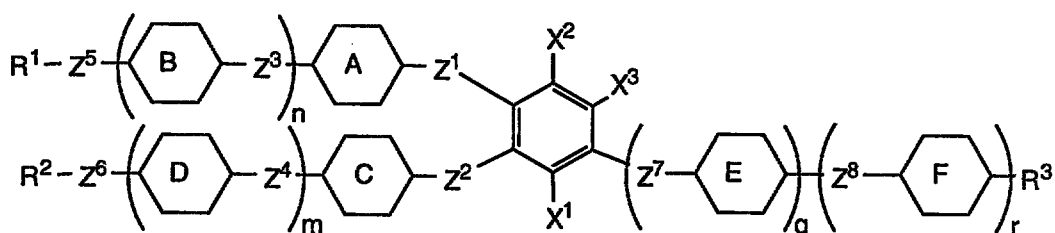
signifies lower alkyl;

R''

signifies methyl, methoxy, cyano or
 halogen, with the proviso that R¹-Z⁵ and
 R²-Z⁶ contain no -O-O- or -N-O- groups;
 R³ signifies hydrogen, halogen, cyano or an
 alkyl, alkoxy, alkoxycarbonyl or alkanoyl-
 oxy group optionally substituted with
 methoxy, cyano and/or halogen; and
 X¹, X² and X³ independently signify hydrogen, halogen,
 cyano or lower alkyl,

whereby the two rings B and D can be the same or different when
 m is 2 and/or n is 2.

2. Compounds according to claim 1 of formula I



wherein

rings A - F

each signify pyridine-2,5-diyl, pyri-
 midine-2,5-diyl, trans-1,4-cyclohexylene,
 trans-1,3-dioxane-2,5-diyl or independ-
 ently of one another 1,4-phenylene



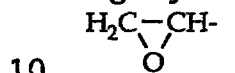
		optionally substituted with halogen, methyl and/or cyano;
	Z ¹ , Z ² and Z ⁷	independently of one another signify -CH ₂ CH ₂ -, -CH ₂ O-, -COO-, -OOC-, -(CH ₂) ₄ - or -(CH ₂) ₃ O-;
5		
	Z ³ , Z ⁴ and Z ⁸	independently of one another signify a single bond, -CH ₂ CH ₂ -, -CH ₂ O-, -OCH ₂ -, -COO-, -OOC-, -(CH ₂) ₄ -, -O(CH ₂) ₃ - or -(CH ₂) ₃ O-;
10	Z ⁵ and Z ⁶	signify -(CY ₂) _s -, -O(CY ₂) _s -, -(CY ₂) _s O-, -(CY ₂) _s COO-, -(CY ₂) _s OOC-, -(Si[(CH ₃) ₂]O) _s -, -OCH ₂ (Si[(CH ₃) ₂]O) _s Si[(CH ₃) ₂]CH ₂ O- or -NHCH ₂ (Si[(CH ₃) ₂]O) _s Si[(CH ₃) ₂]CH ₂ NH-;
	Y	signifies hydrogen or fluorine;
15	m, n, q and r	independently of one another signify 0 or 1;
	s	signifies a whole number of 1 to 16;
	R ¹ and R ²	signify cross-linkable groups 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-,
20		
25		
	Ph	signifies phenyl;
30	R'	signifies lower alkyl;
	R''	signifies methyl, methoxy, cyano or halogen, with the proviso that R ¹ -Z ⁵ and R ² -Z ⁶ contain no -O-O- or -N-O- groups;
	R ³	signifies hydrogen, halogen, cyano or an



5 X^1, X^2 and X^3

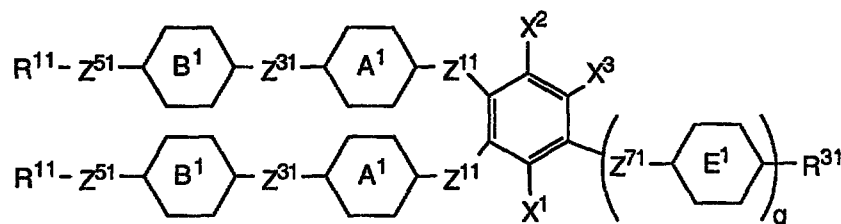
alkyl, alkoxy or alkanoyloxy group
optionally substituted with methoxy,
cyano and/or halogen; and
independently signify hydrogen, halogen,
cyano or lower alkyl.

3. Compounds according to claim 1 or 2, wherein the
cross-linkable residues R^1 and R^2 independently of one another
signify $CH_2=CH-COO-$, $CH_2=C(CH_3)-COO-$, $CH_2=CH-O-$ or



4. Compounds according to any one of claims 1 to 3,
wherein X^1, X^2 and X^3 signify hydrogen, fluorine, chlorine, cyano
and methyl.

5. Compounds according to any one of claims 1 to 4 of
general formula IA



I - A

wherein

A^1, B^1 and E^1

independently of one another signify 1,4-
phenylene optionally substituted with
fluorine, pyridine-2,5-diyl, pyrimidine-
2,5-diyl or trans-1,4-cyclohexylene;

Z^{11}

signifies $-CH_2CH_2-$, $-CH_2O-$, $-COO-$, $-OOC-$,
 $-(CH_2)_4-$ or $-(CH_2)_3O-$;

Z^{31}

signifies a single bond, $-CH_2O-$, $-COO-$ or
 $-OOC-$;

Z^{51}

signifies $-(CH_2)_{s'}-$, $-(CH_2)_{s'}O-$,
 $-(CH_2)_{s'}COO-$ or $-(CH_2)_{s'}OOC-$;

Z^{71}

signifies $-CH_2O-$ or $-COO-$;

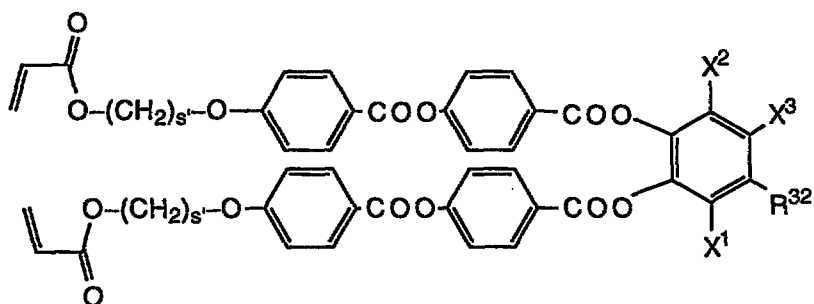
s'

signifies a whole number of 3 to 12;

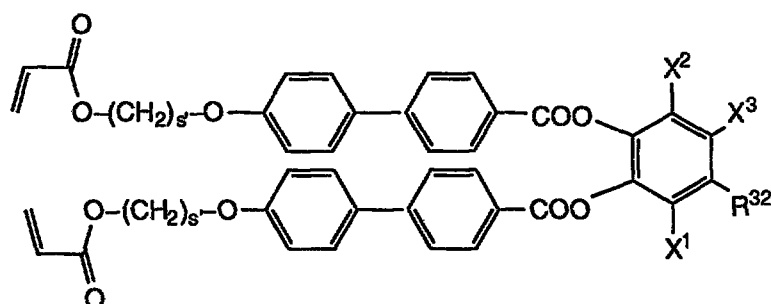


- R¹¹ signifies CH₂=CH-COO-, CH₂=C(CH₃)-COO-,
CH₂=CH-O- or $\begin{matrix} \text{H}_2\text{C}-\text{CH}- \\ | \\ \text{O} \end{matrix}$
- R³¹ signifies halogen, cyano, lower alkyl or
alkoxycarbonyl;
- q signifies 0 or 1; and
- X¹, X² and X³ have the significance given in claim 1.

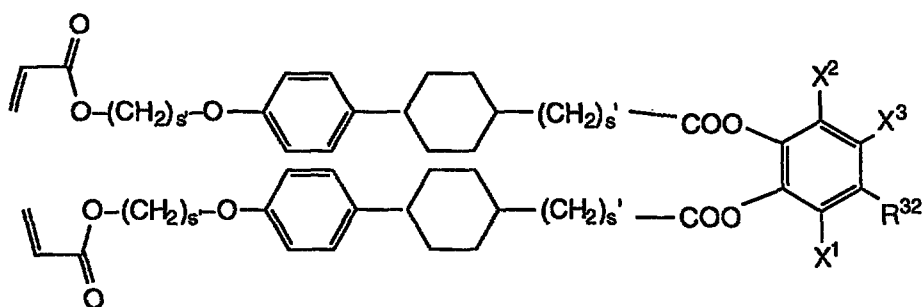
6. Compounds according to claim 5 of formulae Ia-Ic



I - a



I - b

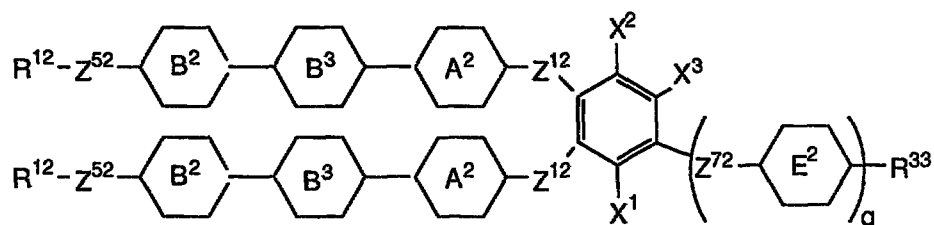


I - c



wherein R³² signifies cyano or alkoxycarbonyl; X¹, X² and X³ signify hydrogen; and s' has the significance given in claim 5.

5 7. Compounds according to any one of claims 1 to 4 of
general formula I-B

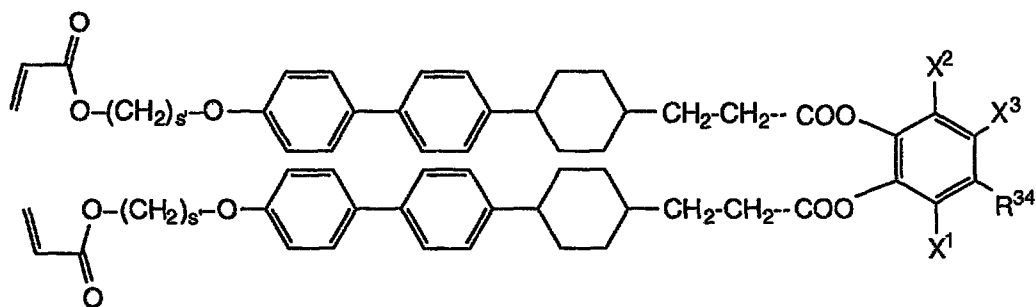


1-B

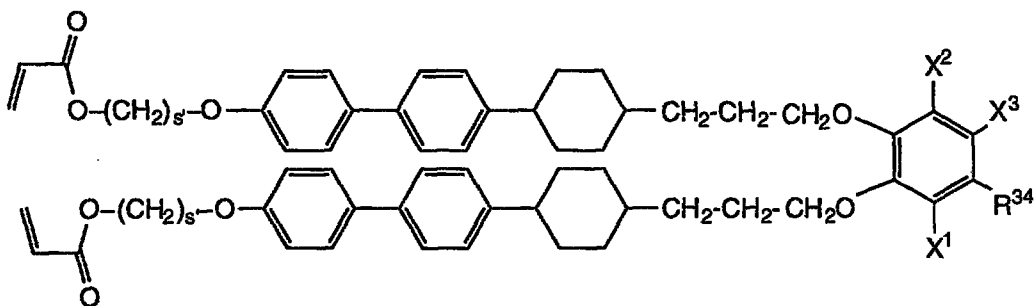
10	wherein	
	A ² , B ² , B ³ and E ²	independently of one another signify 1,4-phenylene optionally substituted with fluorine or trans-1,4-cyclohexylene;
	Z ¹²	signifies -(CH ₂) ₂ COO-, -(CH ₂) _{s'} COO- or
15		-(CH ₂) _{s'} O-;
	Z ⁵²	signifies -(CH ₂) _{s'} -, -(CH ₂) _{s'} O-,
		-(CH ₂) _{s'} COO- or -(CH ₂) _{s'} OOC-;
	Z ⁷²	signifies -CH ₂ O- or -COO- ;
	s'	a whole number of 3 to 12;
20	R ¹²	signifies CH ₂ =CH-COO-, CH ₂ =C(CH ₃)-COO-,
		CH ₂ =CH-O- or $\text{H}_2\text{C}-\underset{\text{O}}{\underset{ }{\text{CH}}}-$
	R ³³	signifies halogen, cyano or alkoxy carbonyl;
	q	signifies 0 or 1; and
	X ¹ , X ² and X ³	have the significance given under claim 1.
25		



8. Compounds according to claim 7 of formulae Id-Ig

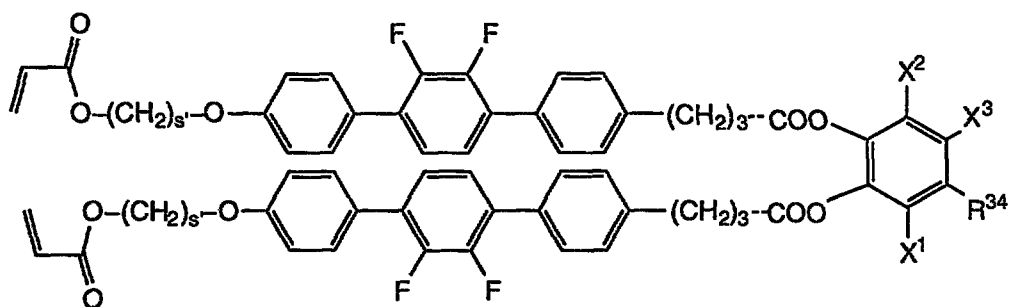


I - d

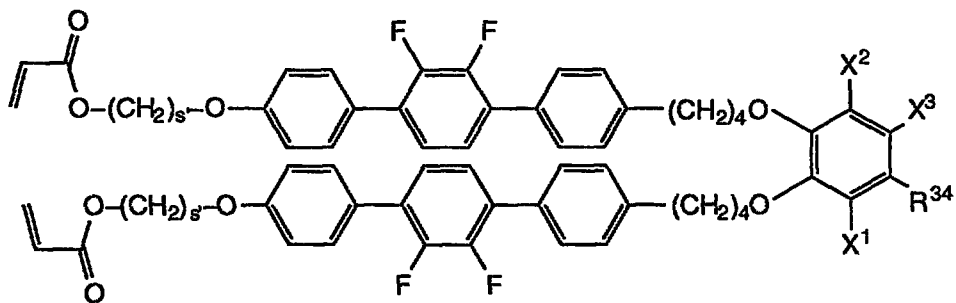


5

I - e



I - f



10

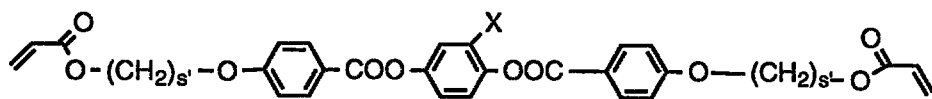
I - g



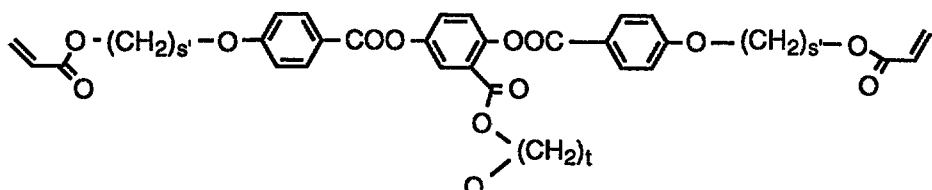
wherein R^{34} signifies cyano or alkoxy carbonyl; X^1 , X^2 and X^3 signify hydrogen; and s' has the significance given in claim 7.

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

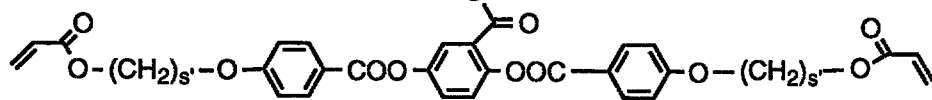
10 10. A cross-linkable liquid crystalline mixture according to claim 9, which contains, in addition to one or more compounds of formula I, one or more compounds from the group of the formulae



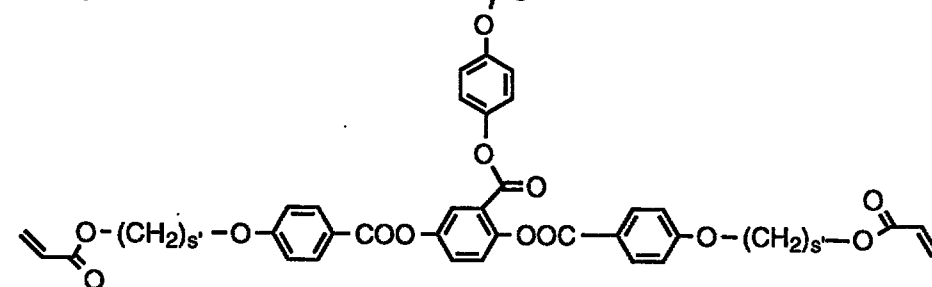
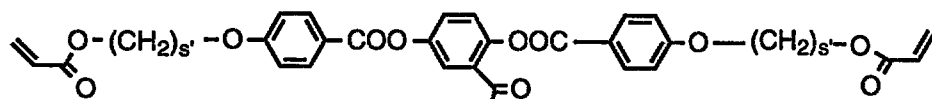
II



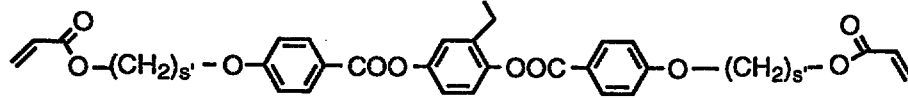
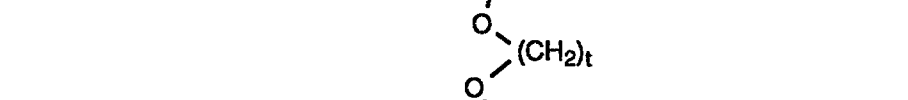
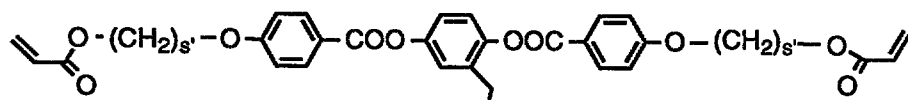
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III



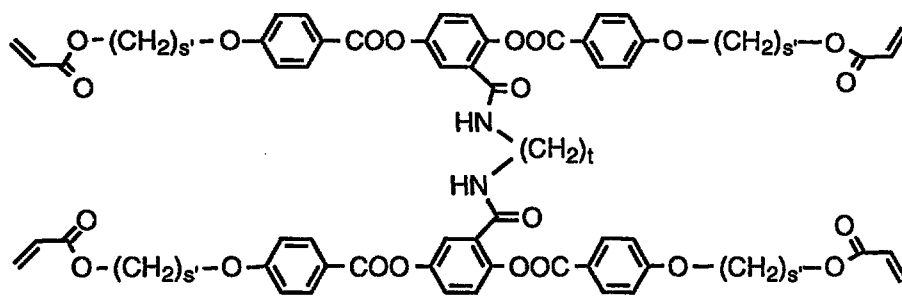
IV



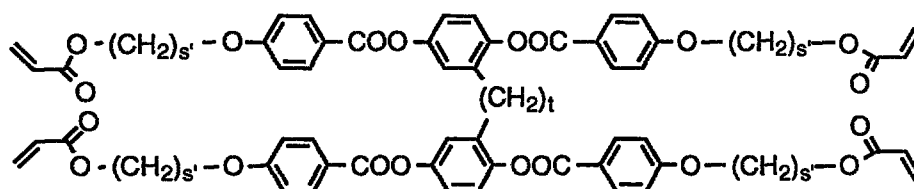
V



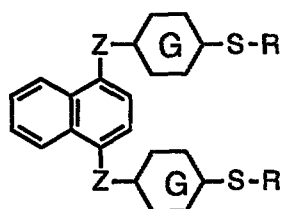
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VI

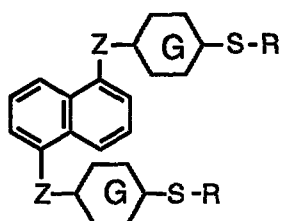


VII



VIII

and



IX

5

wherein

X

signifies hydrogen, fluorine, chlorine, bromine or methyl;

10

s'

signifies a whole number of 3 to 12; and

t

signifies a whole number of 2 to 12;

Z

signifies -OCH₂- or -OOC-;

G

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

15

S

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

R

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



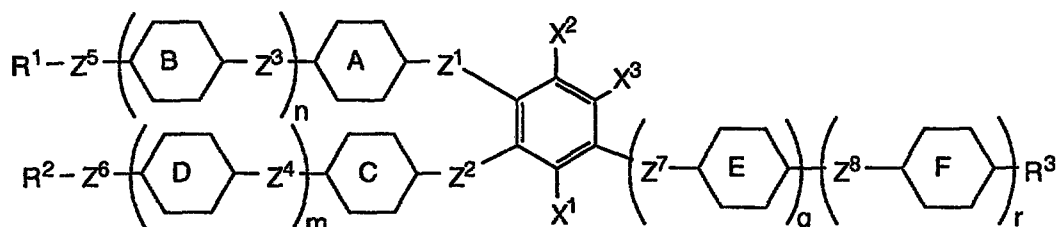
11. The use of compounds according to any one of claims 1 to 8 in their cross-linked state for optical components.

12. The use of cross-linkable liquid crystalline mixtures
5 according to claim 9 or 10 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

I

wherein

rings A - F

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

15

Z¹, Z² and Z⁷

independently of one another signify -CH₂-(CH₂)_s-, -(CH₂)_sO-, -O(CH₂)_s-, -COO-, -OOC-, -(CH₂)_sCOO- or -(CH₂)_sOOC-;

20

Z³, Z⁴ and Z⁸

independently of one another signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;

25

Z⁵ and Z⁶

signify -(CY₂)_s-, -O(CY₂)_s-, -(CY₂)_sO-, -(CY₂)_sCOO-, -(CY₂)_sOOC-, -(Si[(CH₃)₂]O)_s-, -OCH₂(Si[(CH₃)₂]O)_sSi[(CH₃)₂]CH₂O- or -NHCH₂(Si[(CH₃)₂]O)_sSi[(CH₃)₂]CH₂NH-;

30

Y

signifies hydrogen or fluorine;

m, n, q and r

independently of one another signify 0, 1 or 2;

s

signifies a whole number of 1 to 16;

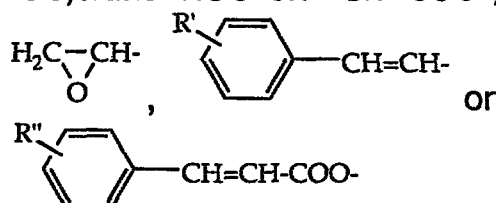
R¹ and R²

signify cross-linkable groups of the

5

structure $\text{CH}_2=\text{CH}-$, $\text{CH}_2=\text{CH}-\text{COO}-$,
 $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-$, $\text{CH}_2=\text{C}(\text{Cl})-\text{COO}-$,
 $\text{CH}_2=\text{C}(\text{Ph})-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{COO}-\text{Ph}-$,
 $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-$,
 $\text{CH}_2=\text{C}(\text{Cl})-\text{CONH}-$, $\text{CH}_2=\text{C}(\text{Ph})-\text{CONH}-$,
 $\text{CH}_2=\text{C}(\text{COOR}')-\text{CH}_2-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{O}-$,
 $\text{CH}_2=\text{CH}-\text{OOC}-$, $\text{Ph}-\text{CH}=\text{CH}-$, $\text{CH}_3-\text{C}(=\text{NR}')$,
 $-\text{cis,trans HOO}-\text{CR}'=\text{CR}'-\text{COO}-$,

10



Ph

signifies phenyl;

R'

signifies lower alkyl;

R''

signifies methyl, methoxy, cyano or
 halogen, with the proviso that R^1-Z^5 and
 R^2-Z^6 contain no $-\text{O}-\text{O}-$ or $-\text{N}-\text{O}-$ groups;

15

R³

signifies hydrogen, halogen, cyano or an
 alkyl, alkoxy, alkoxycarbonyl or
 alkanoyloxy group optionally substituted
 with methoxy, cyano and/halogen; and
 independently signify hydrogen, halogen,
 cyano or lower alkyl,

20

X¹, X² and X³

whereby the two rings B and D can be the same or different when
 m is 2 and/or n is 2, liquid crystalline mixtures which contain
 such compounds and their use in the cross-linked state as optical
 components.

25

PHOTO CROSS-LINKABLE LIQUID CRYSTALLINE 1,2-PHENYLENE-DERIVATIVES

5 The present invention is concerned with photo cross-linkable liquid crystalline 1,2-phenylene derivatives, 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 an appropriate 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, etc. can be produced. Such optical components can be used, for example, for frequency doubling (SHG) or in colour
20 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 optical filters should have a strong absorption in a direction perpendicular to the filter surface.

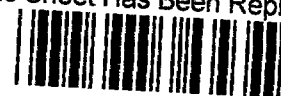
 In addition to the general interest in photo cross-linkable liquid crystals for optical components, such liquid crystalline
30 materials are suitable as a cladding for glass fibres for optical data transmission. The use of such materials increases the elastic modulus in the longitudinal axis of the fibre, lessens the thermal expansion coefficients and thus reduces 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 usual solvents and a good stability towards electric fields and electromagnetic

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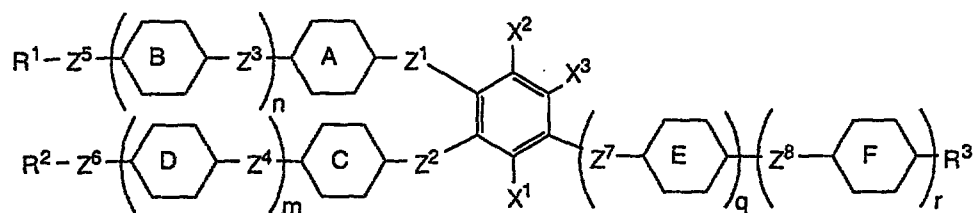


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12 DEC 1996

PHOTO CROSS-LINKABLE LIQUID CRYSTALLINE 1,2-PHENYLENE DERIVATIVESAbstract

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



10

I

wherein

rings A - F

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

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independently of one another signify -CH₂-(CH₂)_s-, -(CH₂)_sO-, -O(CH₂)_s-, -COO-, -OOC-, -(CH₂)_sCOO- or -(CH₂)_sOOC-;

20

Z³, Z⁴ and Z⁸

independently of one another signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;

25

Z⁵ and Z⁶

signify -(CY₂)_s-, -O(CY₂)_s-, -(CY₂)_sO-, -(CY₂)_sCOO-, -(CY₂)_sOOC-, -(Si[(CH₃)₂O]_s)-, -OCH₂(Si[(CH₃)₂O]_sSi[(CH₃)₂]CH₂O- or -NHCH₂(Si[(CH₃)₂O]_sSi[(CH₃)₂]CH₂NH-;

30

Y

signifies hydrogen or fluorine;

m, n, q and r

independently of one another signify 0, 1 or 2;

s

signifies a whole number of 1 to 16;

R¹ and R²

signify cross-linkable groups of the

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PHOTO CROSS-LINKABLE LIQUID CRYSTALLINE 1,2-PHENYLENE
DERIVATIVES

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The present invention is concerned with photo cross-linkable liquid crystalline 1,2-phenylene derivatives, liquid crystalline mixtures which contain such compounds as well as their use in the cross-linked state as optical components.

Photo cross-linkable liquid crystals, which are provided with an appropriate 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 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, etc. can be produced. Such optical components can be used, for example, for frequency doubling (SHG) or in colour filters.

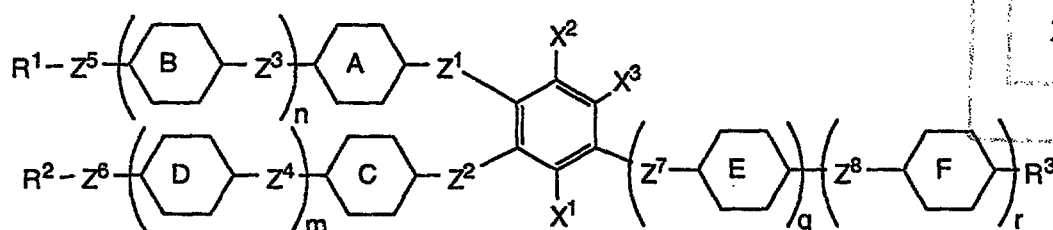
Further properties such as, for example, the birefringence, the refractive index, the transparency, etc. must fulfil different requirements depending on the field of use. For example, materials for optical filters should have a strong absorption in a direction perpendicular to the filter surface.

In addition to the general interest in 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 modulus in the longitudinal axis of the fibre, lessens the thermal expansion coefficients and thus reduces microdistortion losses. This leads to an increased mechanical stability.

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

Abstract

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



wherein

rings A - F

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

Z¹, Z² and Z⁷

independently of one another signify -CH₂-(CH₂)_s-, -(CH₂)_sO-, -O(CH₂)_s-, -COO-, -OOC-, -(CH₂)_sCOO- or -(CH₂)_sOOC-;

Z³, Z⁴ and Z⁸

independently of one another signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;

Z⁵ and Z⁶

signify -(CY₂)_s-, -O(CY₂)_s-, -(CY₂)_sO-, -(CY₂)_sCOO-, -(CY₂)_sOOC-, -(Si[(CH₃)₂]O)_s-, -OCH₂(Si[(CH₃)₂]O)_sSi[(CH₃)₂]CH₂O- or -NHCH₂(Si[(CH₃)₂]O)_sSi[(CH₃)₂]CH₂NH-;

Y

signifies hydrogen or fluorine;

m, n, q and r

independently of one another signify 0, 1 or 2;

s

signifies a whole number of 1 to 16;

R¹ and R²

signify cross-linkable groups of the