

Crosslinkable liquid crystalline compounds

The present invention relates to crosslinkable, especially photocross-linkable, bi-reactive liquid crystalline compounds, to liquid crystalline mixtures comprising such compounds and to the use thereof in the crosslinked state as optical components.

Photocrosslinkable liquid crystals provided with a suitable amount of a photoinitiator can be oriented on a substrate or in a cell by means of suitable orientation layers or in a force field, and can then be crosslinked in that state by irradiation with light of a suitable wavelength. The resulting structure is retained even at high temperatures. Thus, optical components, such as, for example, waveguides, optical gratings, filters and retarders, 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 satisfy different requirements depending on the field of application. For example, materials for optical filters should have high birefringence Δn combined with low dispersion $n = f(\lambda)$.

In addition to the general utility of polymerisable i.e. crosslinkable liquid crystals for optical components, such liquid crystalline materials are suitable for cladding glass fibres for optical data transmission. The use of such materials increases the elastic modulus in the longitudinal axis of the fibre, lowers the thermal expansion coefficients and reduces microdistortion losses. This results in increased mechanical stability. Moreover, crosslinkable liquid crystals have an anisotropic thermal conductivity that enables heat to flow in specific directions.

The crosslinkable liquid crystals must have good chemical and thermal



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stability, good solubility in usual solvents and 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. It is also important that the components have
5 good miscibility with one another since liquid crystals are generally used in the form of mixtures of several components.

For use in optical retarders, polarisation interference filters (for example Solc filters) etc., it is necessary, in addition, for the optical anisotropy to be as great as possible ($\Delta n = |n_e - n_o|$) while the absorption
10 wavelength is as short as possible. In that manner, the desired optical retardation can be obtained with sufficiently thin LCP films (LCP stands for 'liquid crystalline polymer'). The same applies also to use in cholesteric filters, since the band width of the selective reflection is proportional to the optical anisotropy Δn .

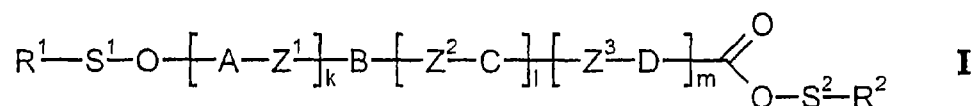
15 Conventional photochemically oligomerisable or polymerisable liquid crystals generally have a high melting point and a high clearing point and medium optical anisotropy. Firstly, the high melting point has the disadvantage that during processing spontaneous thermal polymerisation may occur prematurely at just above the melting point. This spontaneous
20 polymerisation leads to the formation of domains, resulting in significant impairment of the optical and thermal properties of the crosslinked layers produced. Secondly, a small temperature difference between the melting point and the clearing point results in a low degree of ordering and thus in a low degree of optical anisotropy. The melting point can be lowered by
25 producing complex mixtures having several components, which enables processing to be carried out at lower temperatures but entails the risk of crystallisation of conventional polymerisable liquid crystals. Photochemically oligomerisable or polymerisable compounds are described, for example, in EP-A-0 331 233.

30 It is accordingly an object of the present invention to provide

oligomerisable or polymerisable i.e. crosslinkable compounds that, on their own or in mixtures, have an optical anisotropy that is as great as possible while the absorption wavelength is as short as possible, especially for use in optical components. They should also have low melting points and high clearing points so that during processing as high a degree of ordering as possible and thus a high degree of optical anisotropy of the LCP film is obtained at just above the melting point. It should further be possible to orient and structure the compounds without domains, and they should also have excellent thermal stability and long-term stability in the crosslinked state. Conventional photochemically oligomerisable or polymerisable liquid crystals generally have only medium optical anisotropy.

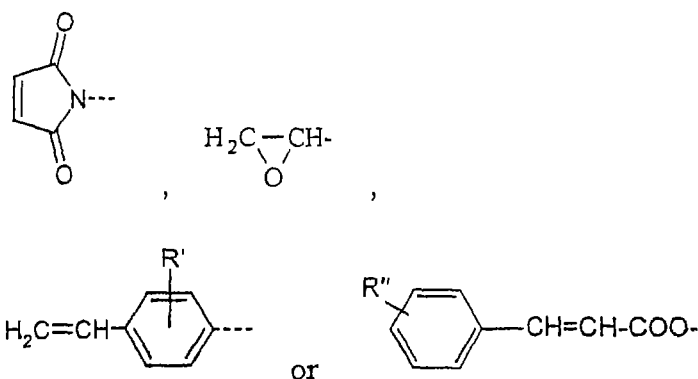
The present invention now provides compounds that are outstandingly suitable as individual components or as components of liquid crystal mixtures for the above-mentioned applications.

The present invention relates to compounds of the general formula I:



wherein

R^1, R^2 each independently of the other represents a crosslinkable group, such as $CH_2=CH-$, $CH_2=CH-COO-$, $CH_2=C(CH_3)-COO-$, $CH_2=C(Cl)-COO-$, $CH_2=C(Ph)-COO-$, $CH_2=CH-COO-Ph-$, $CH_2=CH-CO-NH-$, $CH_2=C(CH_3)-CONH-$, $CH_2=C(Cl)-CONH-$, $CH_2=C(Ph)-CONH-$, $CH_2=C(COOR')-CH_2-COO-$, $(R'OOC)-CH_2-C=CH_2-COO-$, $CH_2=CH-O-$, $CH_2=CH-OOC-$, $CH=CH-Ph-$, *cis*- or *trans*- $HOO-CR'=CR'-COO-$, siloxane,



wherein (Ph) represents phenyl, Ph represents phenylene, R' represents lower alkyl and R'' represents methyl, methoxy, cyano or halogen;

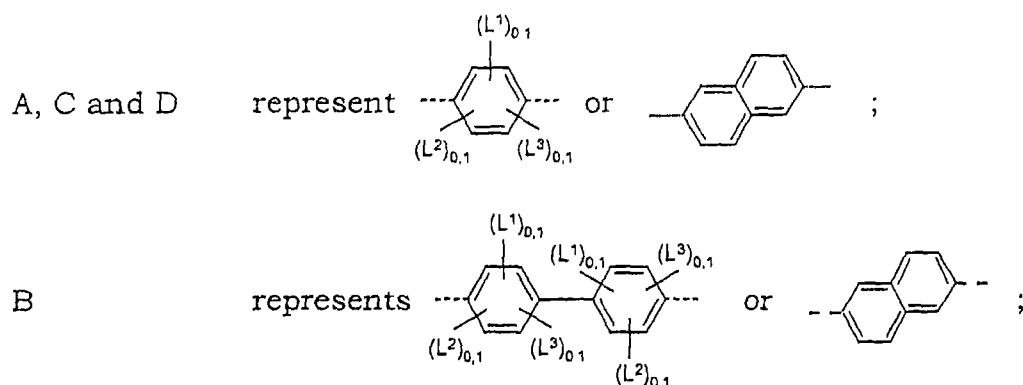
S^1, S^2

each independently of the other represents a spacer unit, such as a straight-chain or branched alkylene grouping $-(\text{CH}_2)_r-$ which may optionally be mono- or poly-substituted by fluorine, or $-((\text{CH}_2)_2-\text{O})_r-$, or a chain of the formula

$-(\text{CH}_2)_r-\text{Y}-(\text{CH}_2)_s-$ which may optionally be mono- or poly-substituted by fluorine, wherein Y is a single bond or a linking functional group, such as $-\text{O}-$, $-\text{COO}-$, $-\text{OOC}-$, $-\text{NR}^3-$, $-\text{NR}^3-\text{CO}-$, $-\text{CO}-\text{NR}^3-$, $-\text{NR}^3-\text{COO}-$, $-\text{OCO}-\text{NR}^3-$, $-\text{NR}^3-\text{CO}-\text{NR}^3-$, $-\text{O}-\text{OC}-\text{O}-$, $-\text{CH}=\text{CH}-$, $-\text{C}\equiv\text{C}-$, wherein R^3

represents hydrogen or lower alkyl and r and s are each an integer from 0 to 20, with the proviso that $2 \leq r + s \leq 20$, or $-(\text{Si}[(\text{CH}_3)_2\text{O}]_u)-$, $-\text{O}(\text{CH}_2)_t(\text{Si}[(\text{CH}_3)_2\text{O}]_u\text{Si}[(\text{CH}_3)_2](\text{CH}_2)_t\text{O}-$, or $-\text{NH}(\text{CH}_2)_t(\text{Si}[(\text{CH}_3)_2\text{O}]_u\text{Si}[(\text{CH}_3)_2](\text{CH}_2)_t\text{NH}-$, wherein t is an integer from 1 to 12 and u is an integer from 1 to 16, with the proviso that $2t + u \leq 20$;

with the proviso that $\text{R}^1 - \text{S}^1$ and $\text{R}^2 - \text{S}^2$ do not contain any $-\text{O}-\text{O}-$ or $-\text{N}-\text{O}-$ groups;



wherein also at least one of the phenylene rings in A, B, C or D may be replaced by a 1,4-phenylene ring in which one or two non-adjacent CH groups have been replaced by nitrogen; and

L¹, L², L³ each independently of the others represents hydrogen, C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₂₀-alkoxy, C₂-C₂₀-alkenyloxy, C₁-C₂₀-alkoxycarbonyl, formyl, C₁-C₂₀-alkylcarbonyl, C₁-C₂₀-alkylcarbonyloxy or nitro,

with the proviso that in at least one phenylene ring in A, B, C or D one of the mentioned substituents is other than hydrogen;

k, l, m are 0 or 1, wherein k + l + m must be equal to 1 or 2; and

Z¹, Z², Z³ each independently of the others represents a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -CH=CH-COO-, -OOC-CH=CH-, -(CH₂)₄-, -O(CH₂)₃-, -(CH₂)₃O- or -C≡C-.

In the structural formulae of the present Application, broken lines (- - - or ———) are used to denote linkages with the adjacent element by a single bond.

Where necessary, the above-used terms will be explained hereinafter.

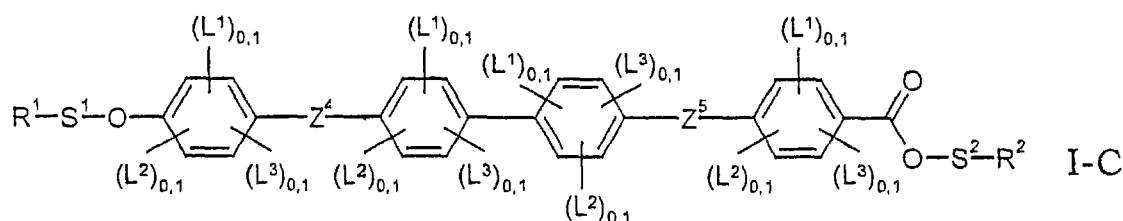
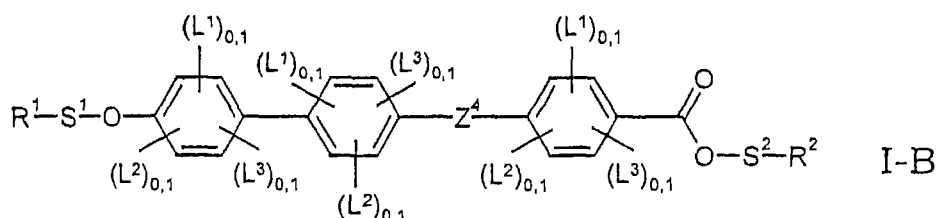
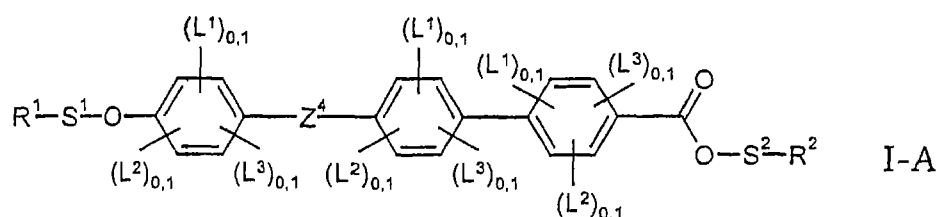
"Lower alkyl" represents, in the context of the present invention, a straight-chain or branched alkyl group having from 1 to 4 carbon atoms, such as, for example, methyl, ethyl, propyl, butyl, isopropyl, isobutyl, *tert*-butyl, but especially methyl, ethyl, propyl or butyl.

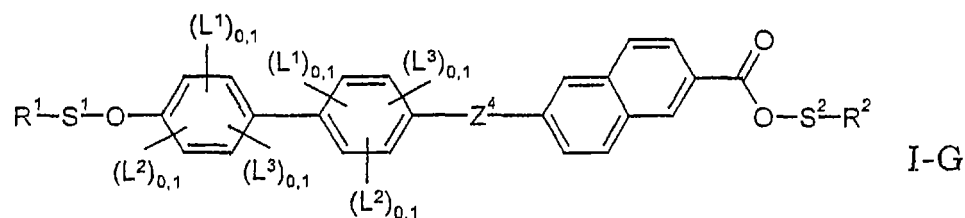
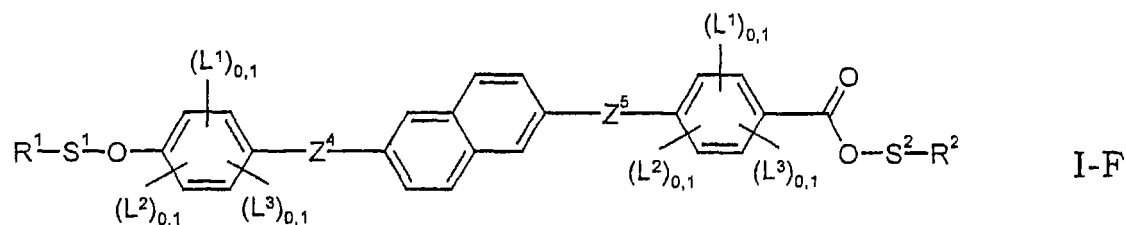
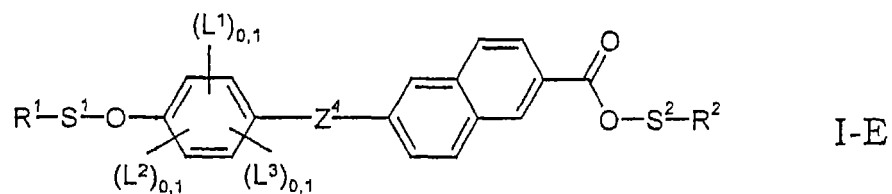
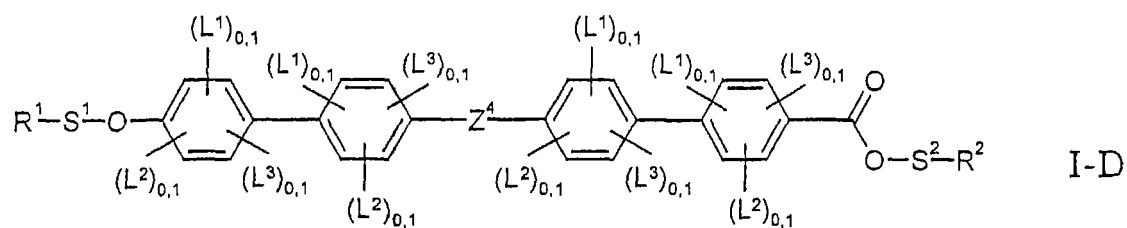
The terms C₂-C₂₀-alkenyl and C₂-C₂₀-alkenyloxy embraces, in the context of the present invention, alkenyl groups having from 2 to 20 carbon atoms, such as 2-alkenyl, 3-alkenyl, 4-alkenyl and alkenyl having a terminal double bond, such as, for example, allyl, 3-butenyl, 4-pentenyl, 5-hexenyl, 6-heptenyl, 7-octenyl, 8-nonenyl, 9-decenyl, 10-undecenyl, allyloxy, 3-butenyloxy, 4-pentenyl, 5-hexenyloxy, 6-heptenyloxy, 7-octenyloxy, 8-nonenyloxy, 9-decenyloxy, 10-undecenyloxy and the like.

When any of L^1 , L^2 , L^3 represents C_2 - C_{20} -alkenyloxy, it may either be a polymerisable group wherein the carbon atom bearing a double bond is directly linked to the oxygen atom, i.e. with the double bond in the 1-position; or a C_3 - C_{20} -alkenyloxy group, wherein the carbon atom bearing a double bond is not directly linked to the oxygen atom.

Such compounds have a surprisingly high degree of optical anisotropy (Δn). Moreover, as components in suitable mixtures they bring about good orientability on orientation layers, which is important, for example, for good contrast.

10 Preferred compounds of formula I are compounds of formulae I-A to I-G





5 wherein

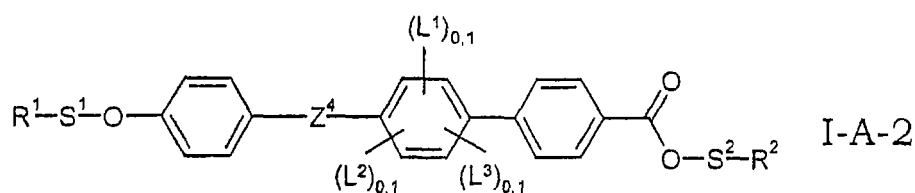
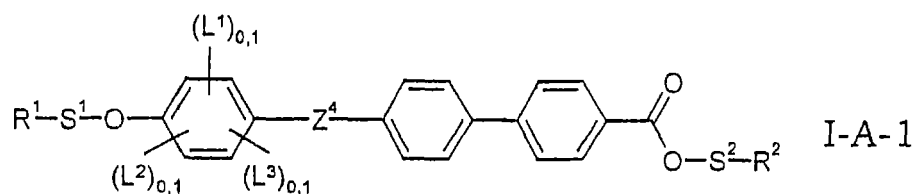
Z^4, Z^5 each independently of the other represents a single bond,
 $-C\equiv C-$, $-COO-$ or $-CH=CH-COO-$; and

$R^1, R^2, S^1, S^2, L^1, L^2$ and L^3
 are as defined for formula I.

10

Special preference is given to the compounds of formulae I-A, I-B, I-D,
 I-F and I-G.

Of the compounds of formula I-A, special preference is given to the compounds of formulae I-A-1 and I-A-2



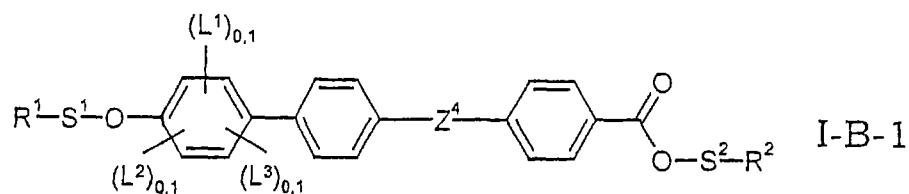
5 wherein

L^1, L^2, L^3 each independently of the others represents hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy or C_2 - C_{20} -alkenyloxy, wherein at least one substituent must be other than hydrogen;

10 Z^4 represents $-C\equiv C-$, $-COO-$, $-CH=CH-COO-$, especially $-COO-$ or $-CH=CH-COO-$, more especially $-COO-$; and

R^1, R^2, S^1, S^2 are as defined for formula I.

15 Of the compounds of formula I-B, special preference is given to the compounds of formula I-B-1



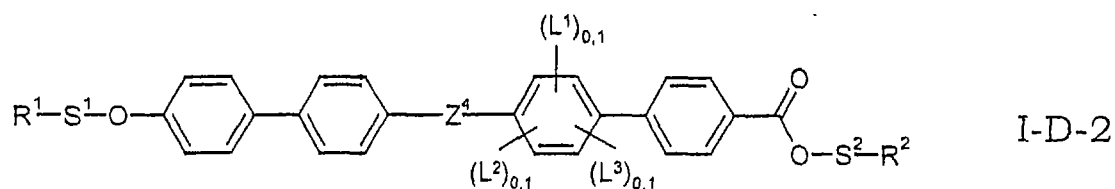
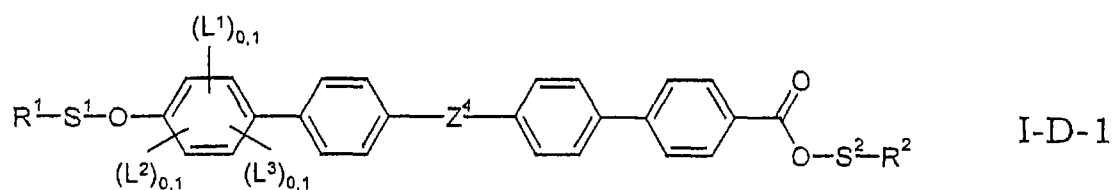
wherein

$R^1, R^2, S^1, S^2, Z^4, L^1, L^2, L^3$

are as defined for formula I-A-1.

5

Of the compounds of formula I-D, special preference is given to the compounds of formulae I-D-1 and I-D-2:

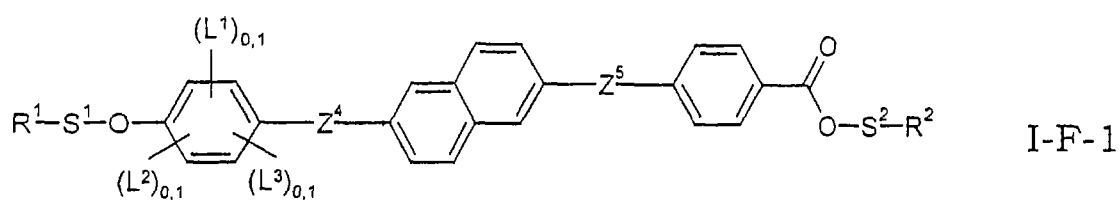


10 wherein

$R^1, R^2, Z^4, L^1, L^2, L^3$

are as defined for formula I-A-1.

15 Of the compounds of formula I-F, special preference is given to the compounds of formula I-F-1

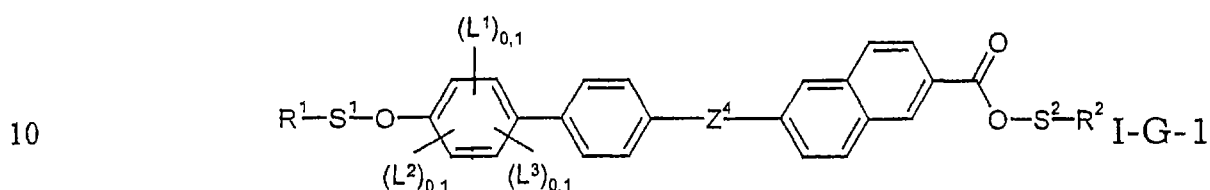


wherein

Z^5 represents a single bond, $-\text{COO}-$ or $-\text{CH}=\text{CH}-\text{COO}-$, especially a single bond; and

5 $R^1, R^2, Z^4, L^1, L^2, L^3$
are as defined for formula I-A-1.

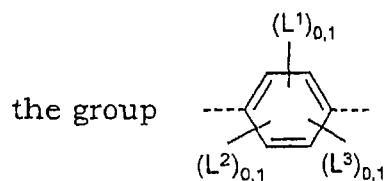
Of the compounds of formula I-G, special preference is given to the compounds of formula I-G-1

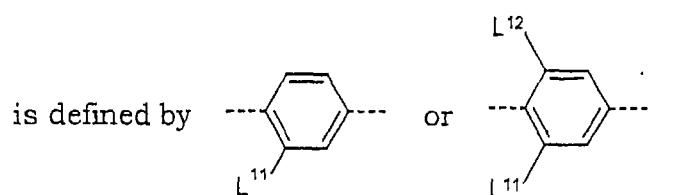


wherein

$R^1, R^2, Z^4, L^1, L^2, L^3$
are as defined for formula I-A-1.

15 More especially preferred compounds of formulae I-A-1, I-A-2, I-B-1, I-D-1, I-D-2, I-F-1 and I-G-1 are those wherein





wherein L^{11} , L^{12} each independently of the other represents C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy or C_2 - C_{20} -alkenyloxy, especially C_1 - C_{12} -alkoxy.

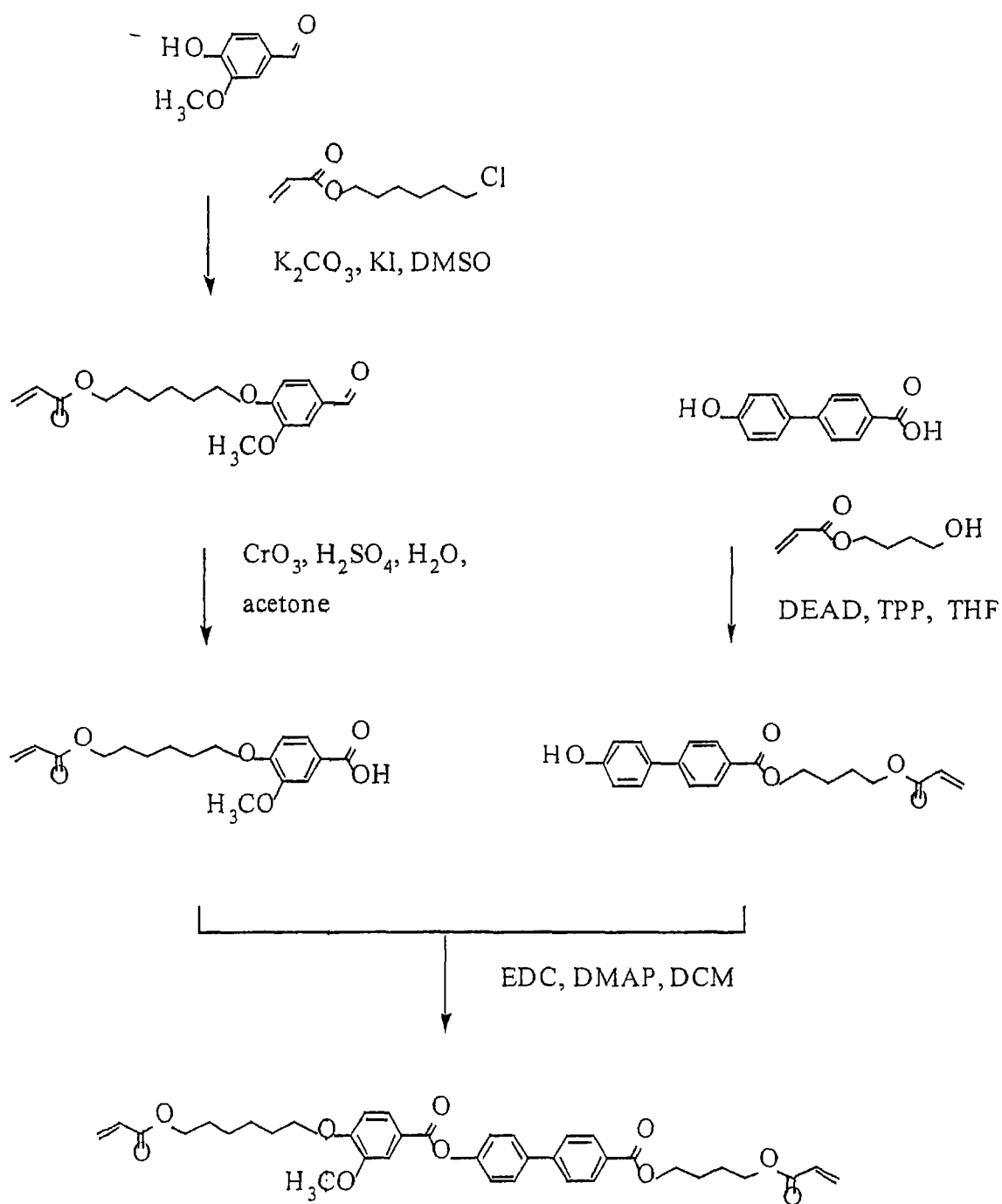
5

The compounds of formula I according to the invention are very easy to obtain synthetically. They can be prepared, for example, analogously to the methods shown in the following Schemes in a manner known *per se*.

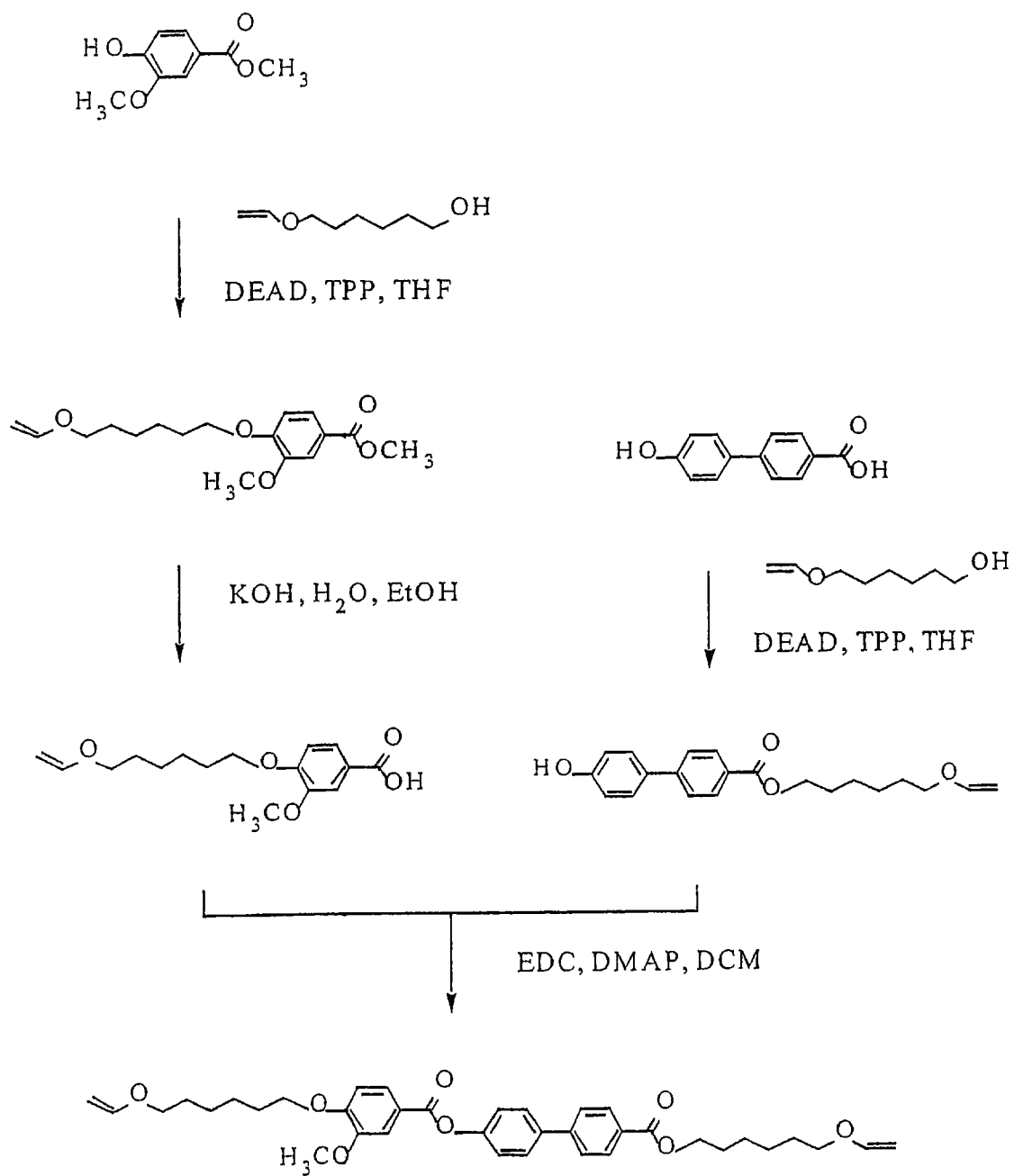
The following abbreviations are used:

10	DCM	dichloromethane
	DME	dimethoxyethane
	DMSO	dimethyl sulphoxide
	THF	tetrahydrofuran
15	EDC	<i>N</i> -(3-dimethylaminopropyl)- <i>N'</i> -ethylcarbodiimide hydrochloride
	DEAD	azodicarboxylic acid diethyl ester (diethyl azodicarboxylate)
	DMAP	4-(dimethylamino)pyridine
	TPP	triphenylphosphine

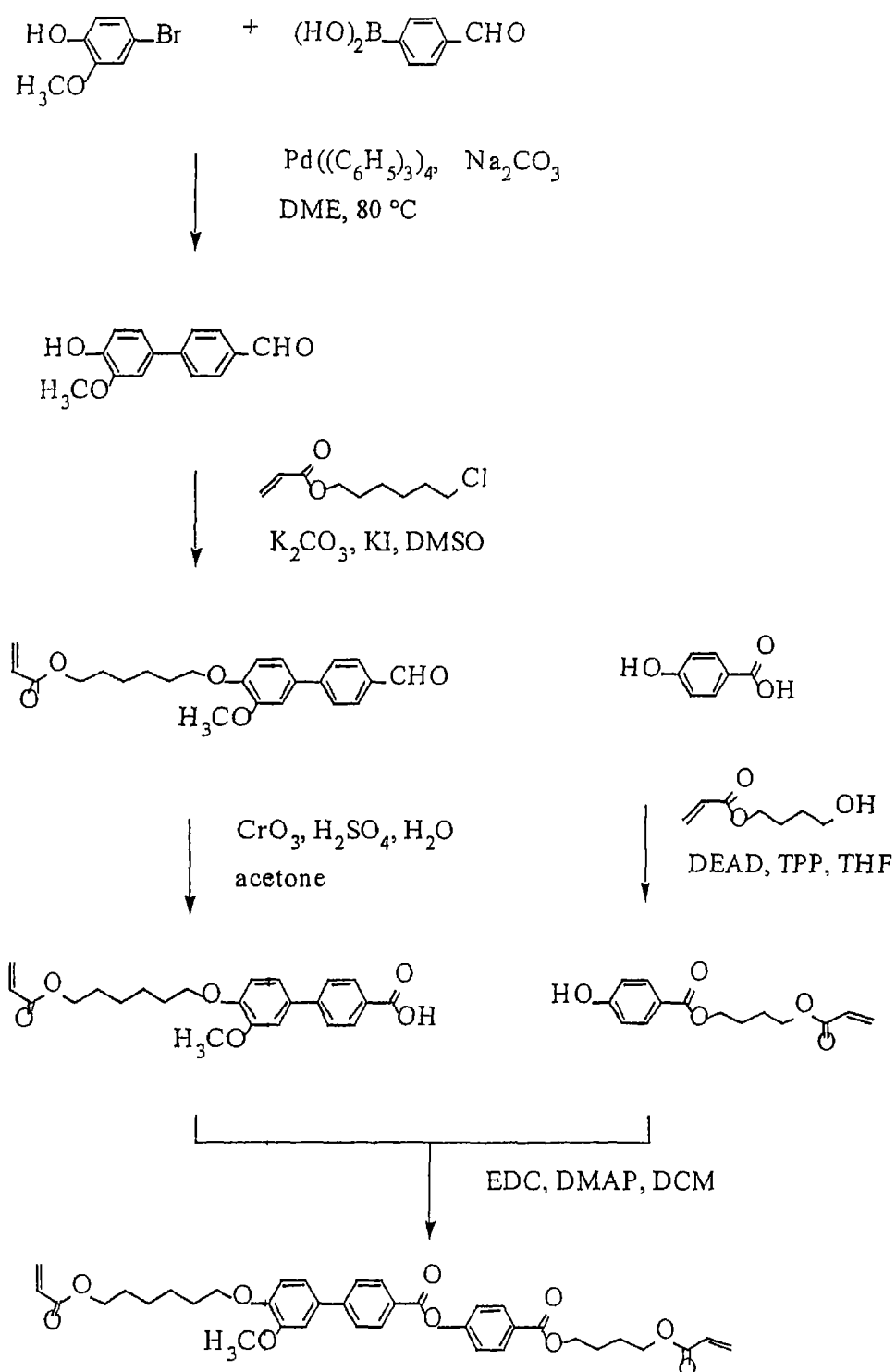
Scheme 1



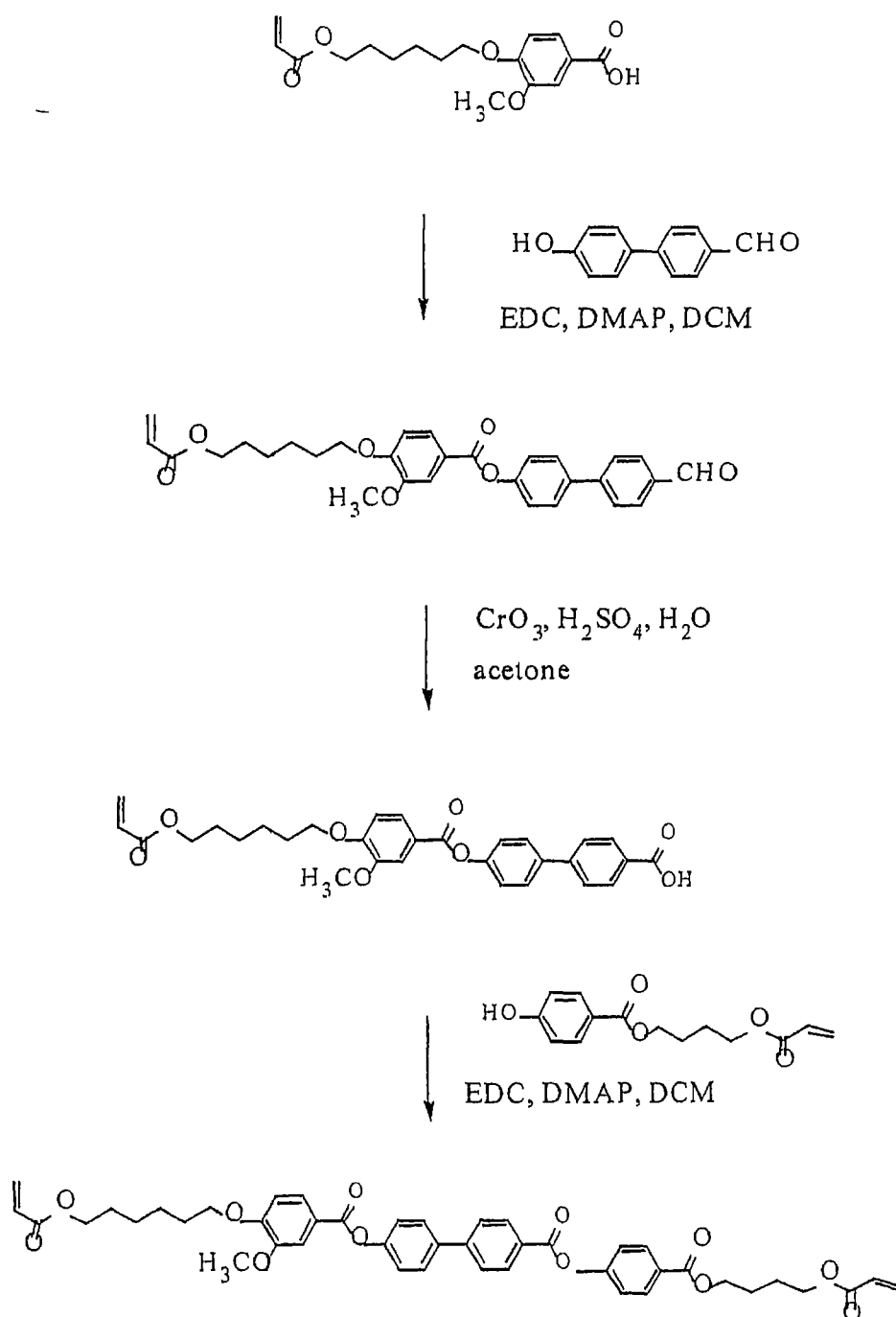
Scheme 2



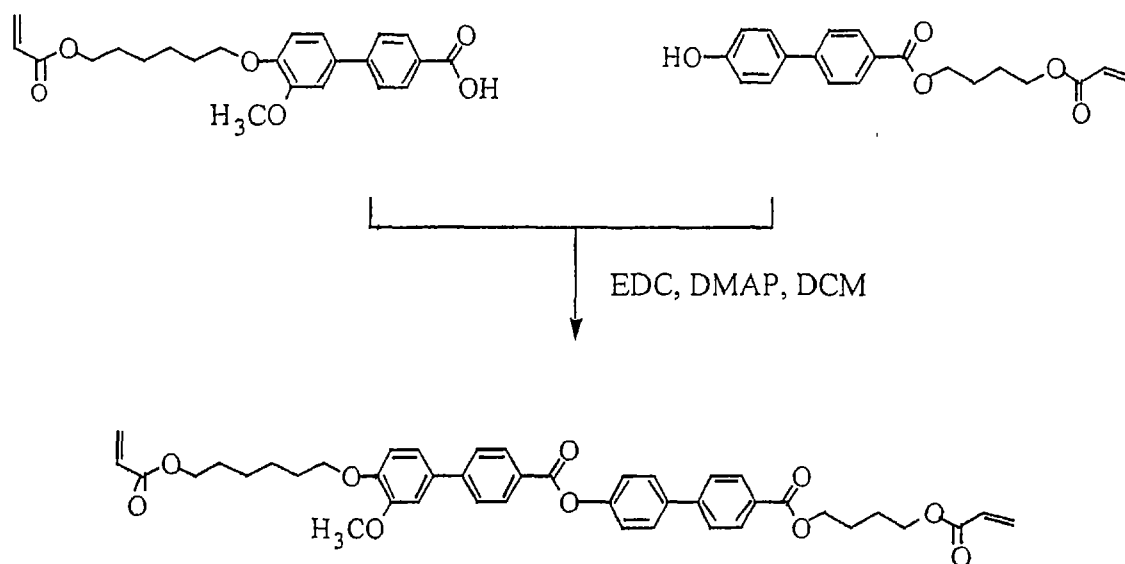
Scheme 3



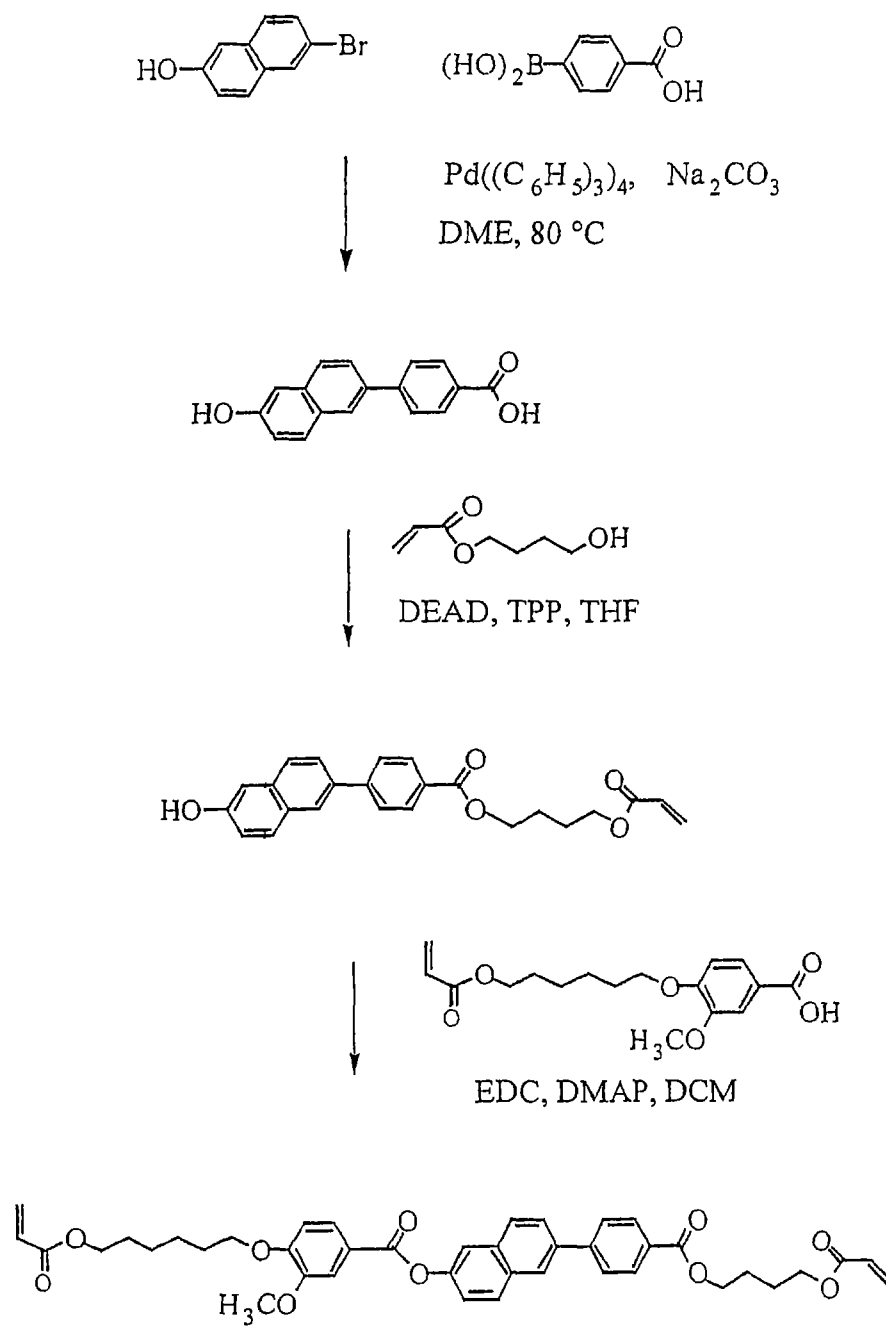
Scheme 4



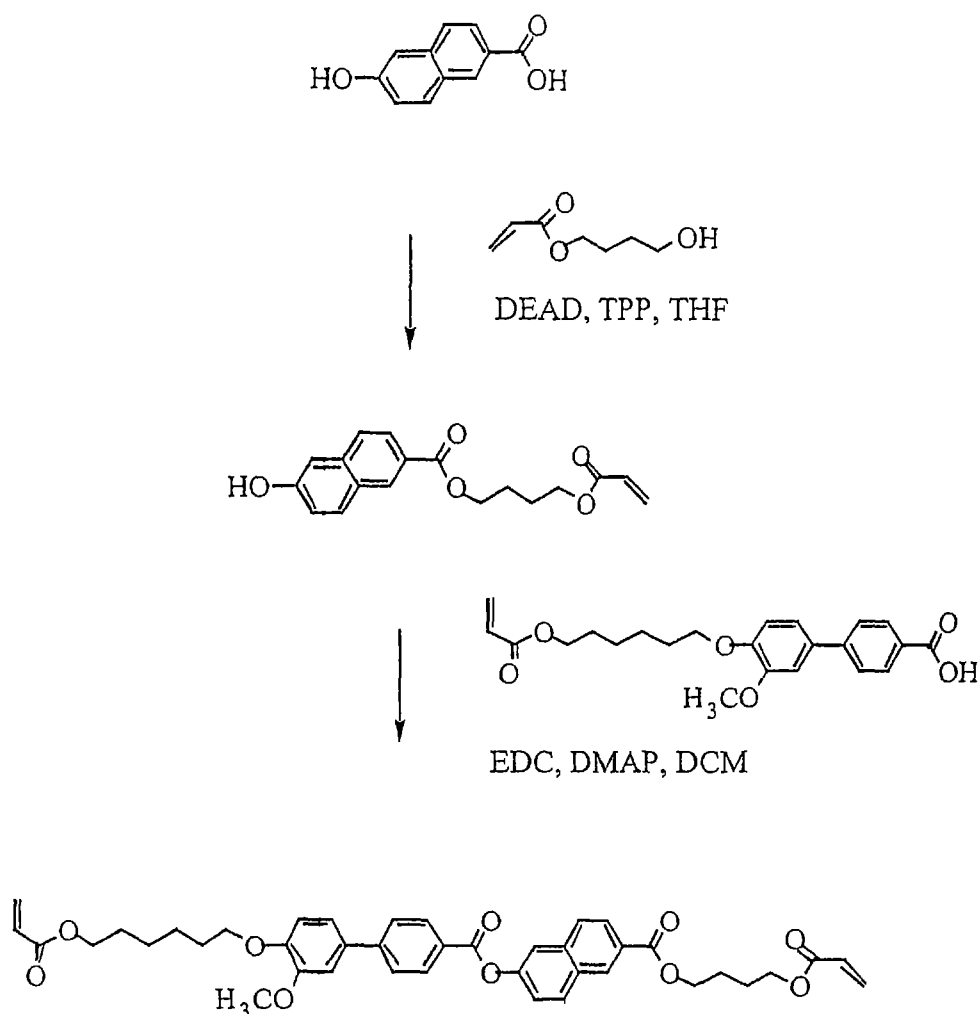
Scheme 5



Scheme 6



Scheme 7



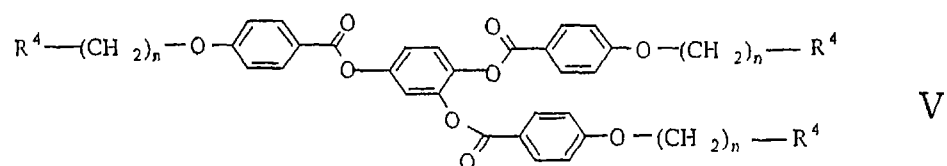
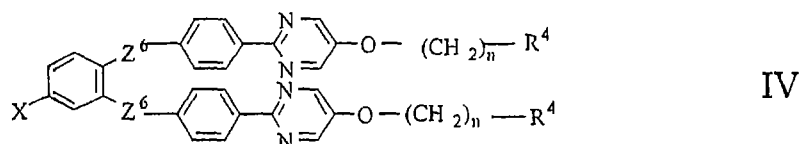
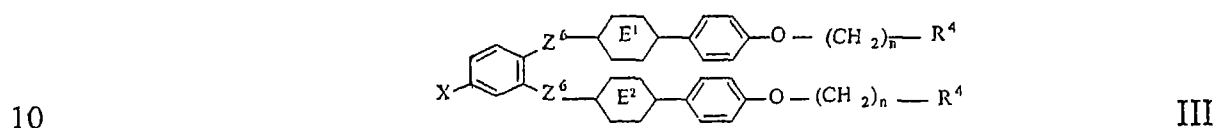
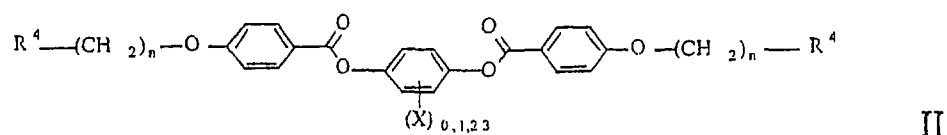
The compounds of formulae I can be used as pure compounds or in the form of mixtures with one another and/or with other liquid crystal components.

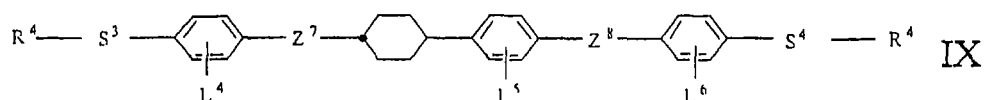
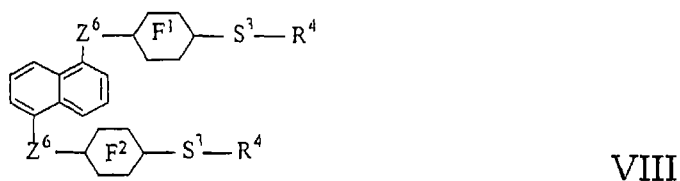
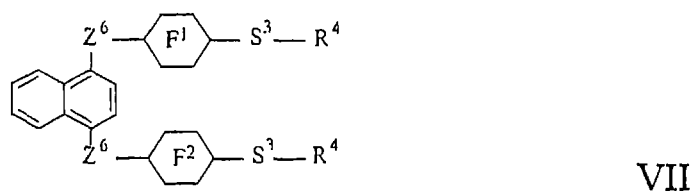
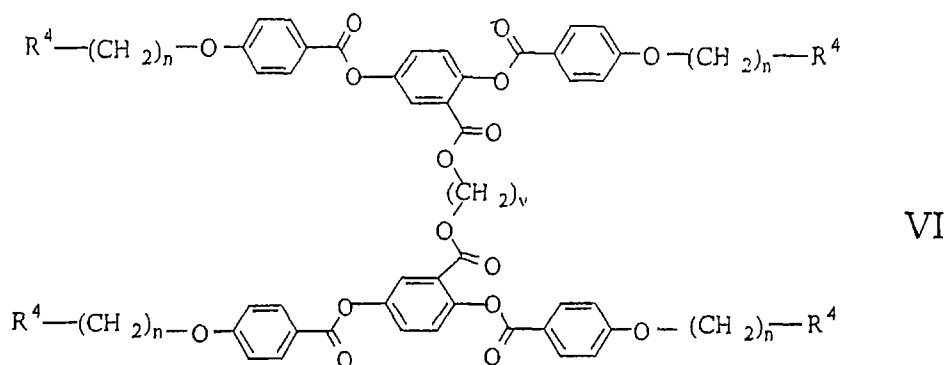
The liquid crystalline mixtures according to the invention comprise at least 2 components, of which at least one component is a compound of formula I. A second component and any further components may be further compounds of formula I or other, known liquid crystalline compounds which may have one or more crosslinkable groups. The mixture may also comprise

one or more chiral components or isotropic doping agents.

By virtue of the good solubility of the compounds of formula I and by virtue of their good miscibility with one another, the proportion of compounds of formula I in the mixtures according to the invention may be high and may be up to 99% by weight.

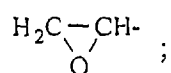
The mixtures according to the invention preferably comprise, in addition to one or more compounds of formula I, one or more compounds from the group of compounds of the general formulae





5 wherein

R^4 represents a polymerisable group, such as $CH_2=CH-$,
 $CH_2=CH-O-$, $CH_2=CH-COO-$, $CH_2=C(CH_3)-COO-$,
 $CH_2=C(Cl)-COO-$ or



10 S^3, S^4 each independently of the other is $-(CH_2)_n-$ or $-O(CH_2)_n-$;

E^1, E^2 each independently of the other represents 1,4-phenylene,

- trans*-1,4-cyclohexylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl or *trans*-1,4-cyclohexylene-1,4-phenylene;
- F¹, F² each independently of the other represents 1,4-phenylene or 2- or 3-fluoro-1,4-phenylene;
- 5 L⁴, L⁵, L⁶ each independently of the others represents hydrogen, C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₂₀-alkoxy, C₁-C₂₀-alkoxy-carbonyl, formyl, C₁-C₂₀-alkylcarbonyl, C₁-C₂₀-alkylcarbonyloxy, halogen, cyano or nitro;
- 10 Z⁶ represents -COO-, -OOC-, -OCH₂-, -CH₂O-, -O(CH₂)₃-, -OOC(CH₂)₂- or -COO(CH₂)₃- ;
- Z⁷ represents a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃-, -(CH₂)₃O- or -C≡C- ;
- Z⁸ represents a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC- or -C≡C- ;
- 15 each X independently of any other(s) represents hydrogen, C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₂₀-alkoxy, C₁-C₂₀-alkoxycarbonyl, formyl, C₁-C₂₀-alkylcarbonyl, C₁-C₂₀-alkylcarbonyloxy, fluorine, chlorine, bromine, cyano or nitro;
- 20 n is an integer from 2 to 20; and
- v is an integer from 2 to 12.

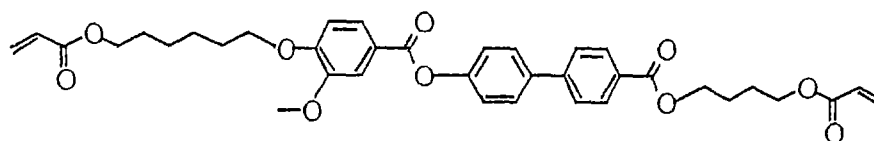
The preparation of the compounds of formula I and liquid crystalline mixtures comprising those compounds is illustrated further by the following

25 Examples. In the Examples, C represents a crystalline phase, N represents a nematic phase, S represents a smectic phase and I represents the isotropic

phase.

Example 1

4'-[4-(6-Acryloyloxyhexyloxy)-3-methoxybenzoyloxy]biphenyl-4-carboxylic
acid 4-acryloyloxybutyl ester



5

1.35 g (7 mmol) of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) are added at 0°C to a solution of 2.38 g (7 mmol) of 4'-hydroxybiphenyl-4-carboxylic acid 4-acryloylbutyl ester, 2.26 g (7 mmol) of 4-(6-acryloyloxyhexyloxy)-3-methoxybenzoic acid and 0.86 g (7 mmol) of 4-dimethylaminopyridine (DMAP) in 180 ml of dichloromethane (DCM). The mixture is stirred for one hour at 0°C and then overnight at room temperature. The reaction mixture is then poured into 300 ml of water and extracted three times with 150 ml of DCM each time. The combined organic phases are washed twice with 200 ml of water each time, dried over magnesium sulphate, filtered and concentrated. Purification of the residue by chromatography on 300 g of silica gel using cyclohexane/ethyl acetate 7:3 and recrystallisation once from 20 ml of ethanol at 0 °C yields 2.58 g of 4'-[4-(6-acryloyloxyhexyloxy)-3-methoxybenzoyloxy]biphenyl-4-carboxylic acid 4-acryloyloxybutyl ester.

20 M.p. (C-S_X) 77 °C, S_X-N 60 °C, Cl. p. (N-I) 62 °C.

The 4'-hydroxybiphenyl-4-carboxylic acid 4-acryloylbutyl ester used as starting material is prepared as follows:

(a) 5.24 g (20 mmol) of triphenylphosphine (TPP) are added at 0°C to a solution of 4.28 g (20 mmol) of 4'-hydroxy-4-biphenylcarboxylic acid and 2.88 g (29 mmol) of 4-hydroxybutyl acrylate in 100 ml of tetrahydrofuran

25

(THF) and then, at the same temperature, 3.50 g (20 mmol) of diethyl azodicarboxylate (DEAD) are added dropwise thereto. The mixture is stirred for one hour at 0°C and then overnight at room temperature. The mixture is then concentrated and the residue is purified by chromatography on silica gel using cyclohexane/ethyl acetate 2:1 to obtain 4.32 g of 4'-hydroxy-biphenyl-4-carboxylic acid 4-acryloylbutyl ester.

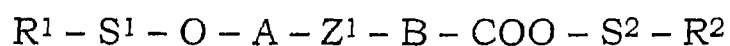
The 4-(6-acryloyloxyhexyloxy)-3-methoxybenzoic acid used as starting material is prepared as follows:

(a) 41.45 g (300 mmol) of potassium carbonate and 27.4 g (165 mmol) of potassium iodide are added to a solution of 22.8 g (150 mmol) of vanillin and 30.7 g (225 mmol) of 6-chlorohexanol in 500 ml of dimethyl sulphoxide (DMSO), and the mixture is stirred overnight at 60°C under nitrogen. The mixture is then cooled to room temperature, poured into 600 ml of water and extracted three times with 150 ml of ethyl acetate each time. The combined organic phases are washed twice with 200 ml of water each time, dried over magnesium sulphate, filtered and concentrated. Purification of the residue by chromatography on 400 g of silica gel using cyclohexane/ethyl acetate 1:1 yields 29.95 g of 4-(6-hexyloxy)-3-methoxybenzaldehyde.

(b) A solution of 97 ml of Jones' reagent is slowly added dropwise at 5°C with ice-cooling to a solution of 27.3 g (89.1 mmol) of 4-(6-hexyloxy)-3-methoxybenzaldehyde in 300 ml of acetone. The mixture is then stirred at room temperature for 2 hours. As soon as the starting material can no longer be detected, the reaction solution is poured into 1 litre of water and 0.3 litre of ethyl acetate. The phases are separated and the aqueous phase is extracted twice with 150 ml of ethyl acetate each time. The combined organic phases are washed with 0.5 litre of water, dried over magnesium sulphate, filtered and concentrated. Purification of the residue by chromatography on silica gel using cyclohexane/ethyl acetate 1:1 and recrystallisation once from ethyl acetate/ether yields 16.7 g of 4-(6-acryloyloxyhexyloxy)-3-methoxybenzoic acid.

Using the appropriate starting compounds, the corresponding compounds are prepared analogously, as shown in Scheme 2, in accordance with reactions known to the person skilled in the art, with vinyl ether as reactive group. Liquid crystals having two different reactive groups can also
5 be synthesised in accordance with the reaction schemes shown.

The following compounds can be prepared in analogous manner:



R ¹	S ¹ -O	A-Z ¹	B	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O				M.p. (C-I) 79 °C
	(CH ₂) ₈ O				
	(CH ₂) ₇ O				
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				
	(CH ₂) ₄ O				
	(CH ₂) ₆ O				

R ^I	S ^I -O	A-Z ^I	B	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O				
	(CH ₂) ₉ O				
	(CH ₂) ₁₀ O				
	(CH ₂) ₆ O				
	(CH ₂) ₃ O				
	(CH ₂) ₆ O				

R ¹	S ¹ -O	A-Z ¹	B	COO-S ² -R ²	Phase transitions
	(CH ₂) ₁₂ O				
	(CH ₂) ₆ O				
	(CH ₂) ₇ O				
	(CH ₂) ₆ O				
	(CH ₂) ₉ O				
	(CH ₂) ₆ O				

R ¹	S ¹ -O	A-Z ¹	B	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				
	(CH ₂) ₇ O				
	(CH ₂) ₆ O				M.p. (C-N) 95 °C, N-I 102 °C
	(CH ₂) ₆ O				

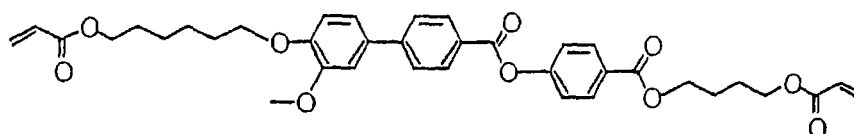
R ^I	S ^I -O	A-Z ^I	B	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O				M.p. (C-S _A) 72 °C, S _A -I 81 °C
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				M.p. (C-S _X) 86 °C, S _X -I 93 °C
	(CH ₂) ₆ O				M.p. (C-I) 66 °C
	(CH ₂) ₆ O				M.p. (C-S _X) 64 °C, S _X -N 77 °C, N-I 83 °C

R ¹	S ¹ -O	A-Z ¹	B	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				
	(CH ₂) ₉ O				
	(CH ₂) ₆ O				
	(CH ₂) ₄ O				
	(CH ₂) ₁₂ O				

R ¹	S ¹ -O	A-Z ¹	B	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O				
	(CH ₂) ₇ O				
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				

Example 2

4'-(6-Acryloyloxyhexyloxy)-3'-methoxybiphenyl-4-carboxylic acid
4-(4-acryloyloxybutoxycarbonyl)phenyl ester

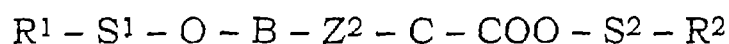


5

The preparation is analogous to Example 1 from 2.64 g (10 mmol) of 4-hydroxybenzoic acid 4-acryloyloxybutyl ester, 3.99 g (10 mmol) of 4'-(6-acryloyloxyhexyloxy)-3'-methoxybiphenyl-4-carboxylic acid, 0.12 g (1 mmol) of DMAP and 2.11 g (11 mmol) of EDC. Purification of the residue by chromatography on silica gel using cyclohexane/ethyl acetate (7:3) and recrystallisation once from ethanol yields 4'-(6-acryloyloxyhexyloxy)-3'-methoxybiphenyl-4-carboxylic acid 4-(4-acryloyloxybutoxycarbonyl)-phenyl ester.

The 4'-(6-acryloyloxyhexyloxy)-3'-methoxybiphenyl-4-carboxylic acid used as starting material is prepared according to a known process by palladium-catalysed boronic acid coupling of 4-bromo-2-methoxyphenol and 4-formylphenylboronic acid, subsequent Williamson etherification of the phenolic hydroxy group with acrylic acid 6-chlorohexyl ester and then oxidation of the aldehyde function to the acid (see Scheme 3).

The following compounds can be prepared in an analogous manner:

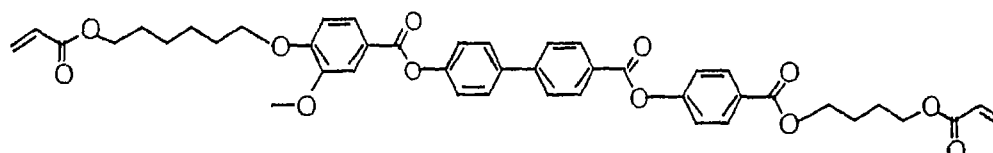


R ¹	SI-O	B	Z ² -C	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O				
	(CH ₂) ₅ O				
	(CH ₂) ₇ O				
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				
	(CH ₂) ₉ O				
	(CH ₂) ₃ O				

R ¹	S ¹ -O	B	Z ² -C	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				
	(CH ₂) ₈ O				
	(CH ₂) ₉ O				
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				
	(CH ₂) ₆ O				

Example 3

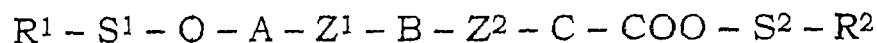
4'-[4-(6-Acryloyloxyhexyloxy)-3-methoxybenzoyloxy]biphenyl-4-carboxylic
acid 4-(6-acryloyloxyhexyloxy)phenyl ester



- 5 The preparation is analogous to Example 1 from 2.64 g (10 mmol) of 4-hydroxybenzoic acid 4-acryloyloxybutyl ester, 5.19 g (10 mmol) of 4'-[4-(6-acryloyloxyhexyloxy)-3-methoxybenzoyloxy]biphenyl-4-carboxylic acid, 0.12 g (1 mmol) of DMAP and 2.11 g (11 mmol) of EDC. Purification of the residue by chromatography on silica gel using cyclohexane/ethyl acetate
10 (7:3) and recrystallisation once from ethanol yields 4'-[4-(6-acryloyloxyhexyloxy)-3-methoxybenzoyloxy]biphenyl-4-carboxylic acid 4-(6-acryloyloxyhexyloxy)phenyl ester.

- The 4'-[4-(6-acryloyloxyhexyloxy)-3-methoxybenzoyloxy]biphenyl-
-4-carboxylic acid used as starting material is prepared as shown in Scheme
15 4 according to methods known to the person skilled in the art from 4-[6-acryloyloxyhexyloxy)-3-methoxybenzoic acid.

The following compounds can be prepared in analogous manner:



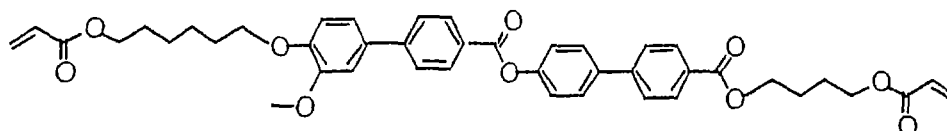
R ¹	S ¹ -O	A-Z ¹	B	Z ² -C	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₅ O					
	(CH ₂) ₈ O					
	(CH ₂) ₆ O					

R ¹	S ¹ -O	A-Z ¹	B	Z ² -C	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₈ O					
	(CH ₂) ₇ O					
	(CH ₂) ₆ O					

R ¹	S ¹ -O	A-Z ¹	B	Z ² -C	COO-S ² -R ²	Phase transitions
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					

Example 4

4'-(6-Acryloyloxyhexyloxy)-3'-methoxybiphenyl-4-carboxylic acid
4'-(4-acryloyloxybutoxycarbonyl)biphenyl-4-yl ester



5

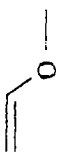
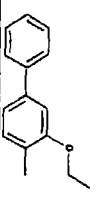
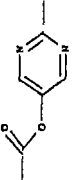
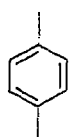
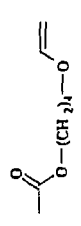
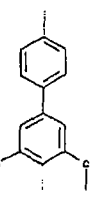
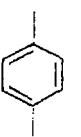
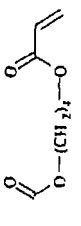
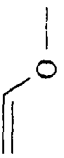
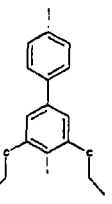
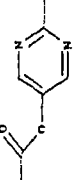
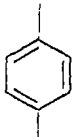
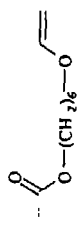
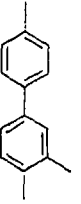
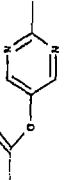
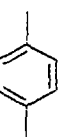
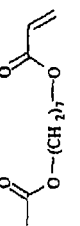
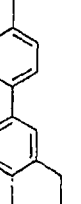
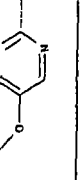
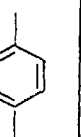
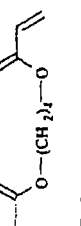
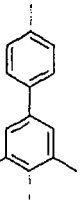
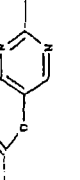
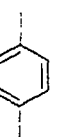
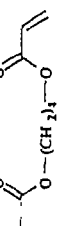
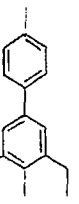
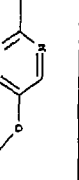
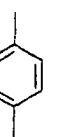
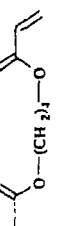
The preparation is analogous to Example 1 from 3.40 g (10 mmol) of 4'-hydroxybiphenyl-4-carboxylic acid 4-acryloylbutyl ester, 3.99 g (10 mmol) of 4'-(6-acryloyloxyhexyloxy)-3'-methoxybiphenyl-4-carboxylic acid, 0.12 g (1 mmol) of DMAP and 2.11 g (11 mmol) of EDC. Purification of the residue
10 by chromatography on silica gel using cyclohexane/ethyl acetate (7:3) and recrystallisation once from ethanol yields 4'-(6-acryloyloxyhexyloxy)-3'-methoxybiphenyl-4-carboxylic acid 4'-(4-acryloyloxybutoxycarbonyl)-biphenyl-4-yl ester.

The following compounds can be prepared in analogous manner:

15 $R^1 - S^1 - O - B - Z^2 - C - Z^3 - D - COO - S^2 - R^2$

R ¹	S ¹ -O	B	Z ² -C	Z ³ -D	-COO-S ² -R ³	Phase transitions
	(CH ₂) ₆ O					
	(CH ₂) ₅ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₁₀ O					
	(CH ₂) ₆ O					
	(CH ₂) ₅ O					
	(CH ₂) ₆ O					

R ¹	S ¹ -O	B	Z ² -C	Z ³ -D	-COO-S ² -R ³	Phase transitions
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₇ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₄ O					

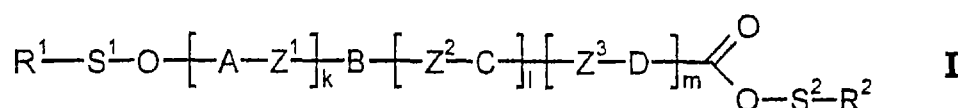
R ¹	S ¹ -O	B	Z ² -C	Z ³ -D	-COO-S ² -R ³	Phase transitions
	(CH ₂) ₆ O					
	(CH ₂) ₆ O					
	(CH ₂) ₅ O					
	(CH ₂) ₆ O					
	(CH ₂) ₉ O					
	(CH ₂) ₆ O					
	(CH ₂) ₃ O					

Example 5

A mixture of 40% by weight of 4'-[4-(6-acryloyloxyhexyloxy)-3-methoxybenzoyloxy]biphenyl-4-carboxylic acid 4-acryloyloxybutyl ester, 40% by weight of 4'-[4-(6-acryloyloxyhexyloxy)-3-ethoxybenzoyloxy]biphenyl-4-carboxylic acid 4-acryloyloxybutyl ester and 20% by weight of 4-(6-acryloyloxyhexyloxy)benzoic acid 4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylphenyl ester is introduced into a parallel cell. The anisotropy of that cell is $\Delta n = 0.2$. The clearing point of the mixture is $T_c = 54.3^\circ\text{C}$, with a phase transition S_A/N being observed at 35.3°C . The mixture can be cooled to below room temperature.

Claims

1. A compound of the general formula I:

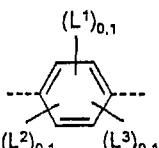
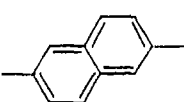


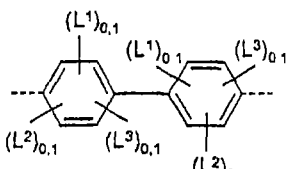
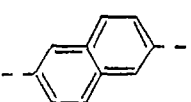
wherein

5 R^1, R^2 each independently of the other represents a crosslinkable group;

S^1, S^2 each independently of the other represents a spacer unit;

with the proviso that R^1-S^1 and R^2-S^2 do not contain any -O-O- or -N-O- groups;

10 A, C and D represent  or  ;

B represents  or  ;

wherein also at least one of the phenylene rings in A, B, C or D may be replaced by a 1,4-phenylene ring in which one or two non-adjacent CH groups have been replaced by nitrogen;
and

15 L^1, L^2, L^3 each independently of the others represents —hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy, C_2 - C_{20} -alkenyloxy, C_1 - C_{20} -alkoxycarbonyl, formyl, C_1 - C_{20} -alkylcarbonyl, C_1 - C_{20} -alkylcarbonyloxy or nitro,

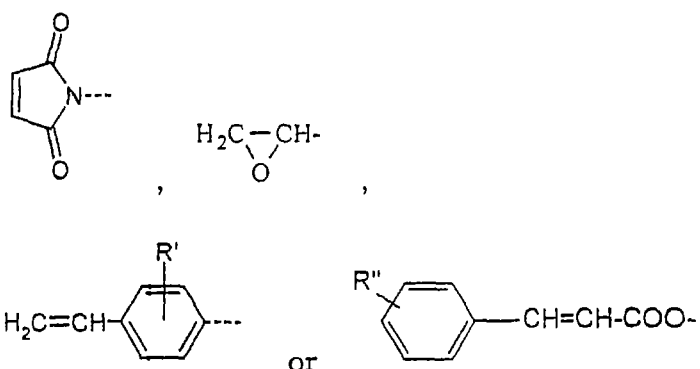
with the proviso that in at least one phenylene ring in A, B, C or D one of the mentioned substituents is other than hydrogen;

k, l, m are 0 or 1, wherein $k + l + m$ must be equal to 1 or 2; and

5 Z^1, Z^2, Z^3 each independently of the others represents a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{OCH}_2-$, $-\text{COO}-$, $-\text{OOC}-$, $-\text{CH}=\text{CH}-\text{COO}-$, $-\text{OOC}-\text{CH}=\text{CH}-$, $-(\text{CH}_2)_4-$, $-\text{O}(\text{CH}_2)_3-$, $-(\text{CH}_2)_3\text{O}-$ or $-\text{C}\equiv\text{C}-$.

2. A compound according to claim 1 wherein

10 R^1, R^2 each independently of the other represents $\text{CH}_2=\text{CH}-$, $\text{CH}_2=\text{CH}-\text{COO}-$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-$, $\text{CH}_2=\text{C}(\text{Cl})-\text{COO}-$, $\text{CH}_2=\text{C}(\text{Ph})-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{COO}-\text{Ph}-$, $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CONH}-$, $\text{CH}_2=\text{C}(\text{Cl})-\text{CONH}-$, $\text{CH}_2=\text{C}(\text{Ph})-\text{CONH}-$, $\text{CH}_2=\text{C}(\text{COOR}')-\text{CH}_2-\text{COO}-$, $(\text{R}'\text{OOC})-\text{CH}_2-\text{C}=\text{CH}_2-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{O}-$, $\text{CH}_2=\text{CH}-\text{OOC}-$,
15 $\text{CH}=\text{CH}-\text{Ph}-$, *cis*- or *trans*- $\text{HOO}-\text{CR}'=\text{CR}'-\text{COO}-$, siloxane,



wherein (Ph) represents phenyl, Ph represents phenylene, R' represents lower alkyl and R'' represents methyl, methoxy, cyano or halogen.

3. A compound according to claim 1 or 2 wherein

S¹, S²

each independently of the other represents a straight-chain or branched alkylene grouping $-(CH_2)_r-$ which may optionally be mono- or poly-substituted by fluorine, or $-((CH_2)_2-O)_r-$, or a chain of the formula $-(CH_2)_r-Y-(CH_2)_s-$ which may optionally be mono- or poly-substituted by fluorine, wherein Y is a single bond or a linking functional group.

5

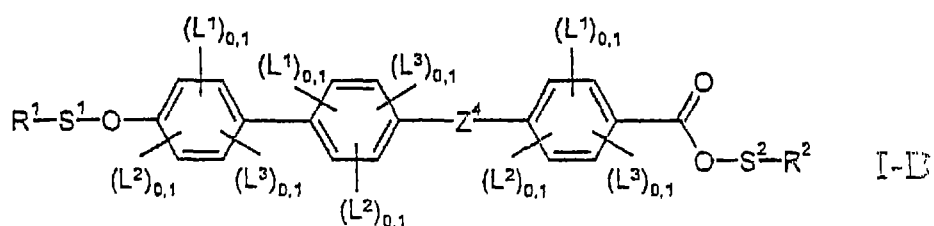
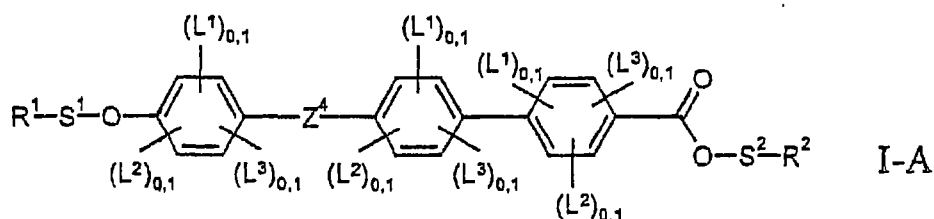
4. A compound according to claim 3 wherein

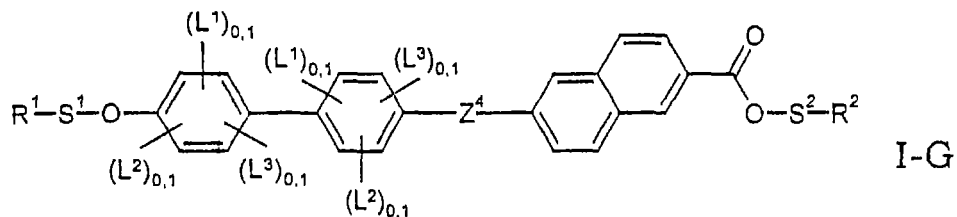
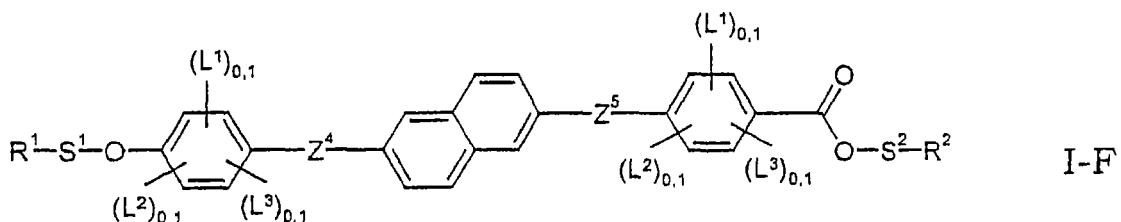
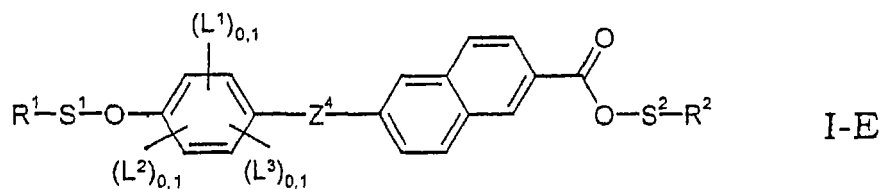
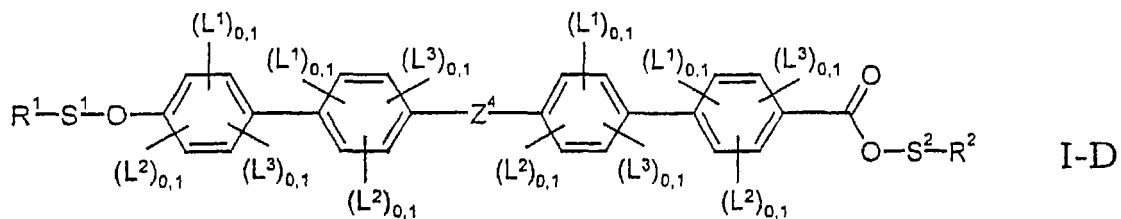
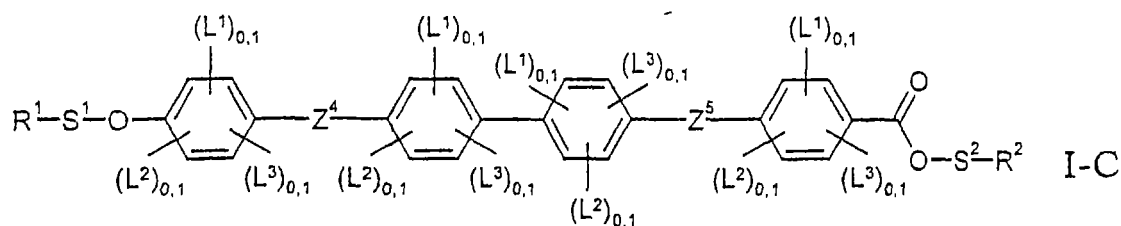
Y is a linking functional group comprising $-O-$, $-COO-$, $-OOC-$, $-NR^3-$, $-NR^3-CO-$, $-CO-NR^3-$, $-NR^3-COO-$, $-OCO-NR^3-$, $-NR^3-CO-NR^3-$, $-O-OC-O-$, $-CH=CH-$, $-C\equiv C-$, wherein R³ represents hydrogen or lower alkyl and r and s are each an integer from 0 to 20, with the proviso that $2 \leq r + s \leq 20$, or $-(Si[(CH_3)_2O]_u)-$, $-O(CH_2)_t(Si[(CH_3)_2O]_u)Si[(CH_3)_2](CH_2)_tO-$ or $-NH(CH_2)_t(Si[(CH_3)_2O]_u)Si[(CH_3)_2](CH_2)_tNH-$, wherein t is an integer from 1 to 12 and u is an integer from 1 to 16, with the proviso that $2t + u \leq 20$.

10

15

5. A compound according to any preceding claim of formulae I-A to I-G



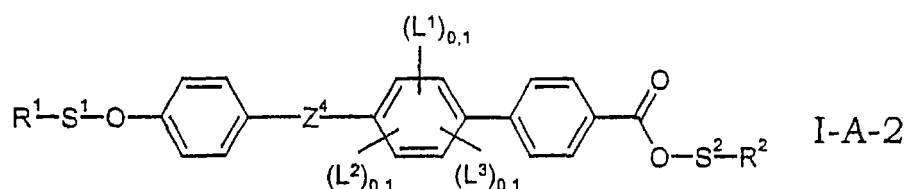
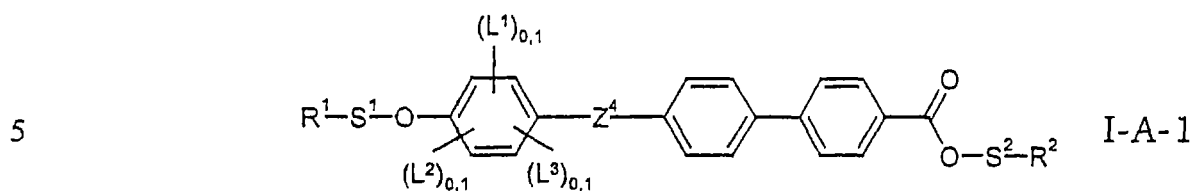


wherein

Z^4, Z^5 — each independently of the other represents a single bond,
 $-C\equiv C-$, $-COO-$ or $-CH=CH-COO-$; and

R^1 , R^2 , S^1 , S^2 , L^1 , L^2 and L^3
are as defined in claim 1.

6. A compound according to any preceding claim of formulae I-A-1 and I-A-2



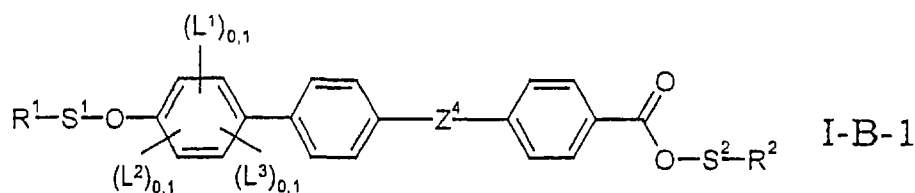
wherein

10 L^1 , L^2 , L^3 each independently of the others represents hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy or C_2 - C_{20} -alkenyloxy, wherein at least one substituent must be other than hydrogen;

Z^4 represents $-C\equiv C-$, $-COO-$, $-CH=CH-COO-$, especially $-COO-$ or $-CH=CH-COO-$, more especially $-COO-$; and

15 R^1 , R^2 , S^1 and S^2 are as defined in claim 1.

7. A compound according to any one of claims 1 to 5 of formula I-B-1



wherein

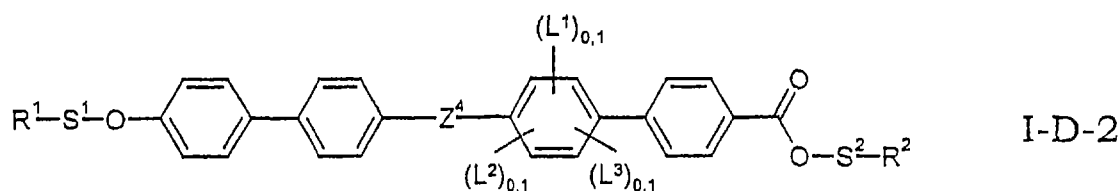
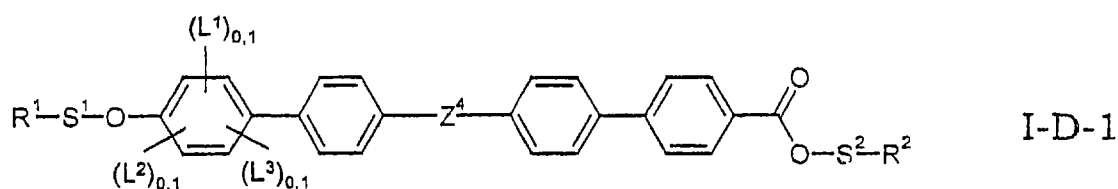
L^1, L^2, L^3 each independently of the others represents hydrogen,
 C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy or
 C_2 - C_{20} -alkenyloxy, wherein at least one substituent must be
 other than hydrogen;

Z^4 represents $-C\equiv C-$, $-COO-$, $-CH=CH-COO-$, especially $-COO-$
 or $-CH=CH-COO-$, more especially $-COO-$; and

R^1, R^2, S^1 and S^2

are as defined in claim 1.

8. A compound according to any one of claims 1 to 5 of formulae I-D-1
 and I-D-2:



wherein

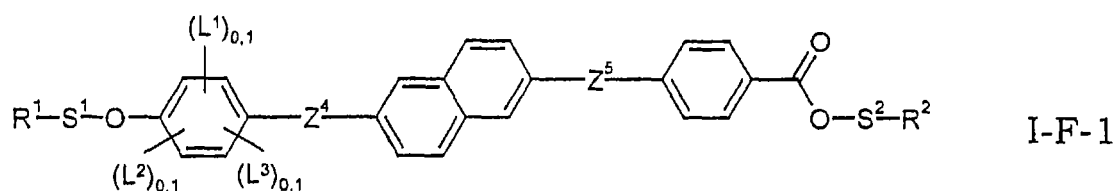
L^1, L^2, L^3 each independently of the others represents hydrogen,

C₁-C₂₀-alkyl, C₆-C₂₀-alkenyl, C₁-C₂₀-alkoxy or
C₂-C₂₀-alkenyloxy, wherein at least one substituent must be
other than hydrogen;

Z⁴ represents -C≡C-, -COO- or -CH=CH-COO-; and

5 R¹, R², S¹ and S²
are as defined in claim 1.

9. A compound according to any one of claims 1 to 5 of formula I-F-1



wherein

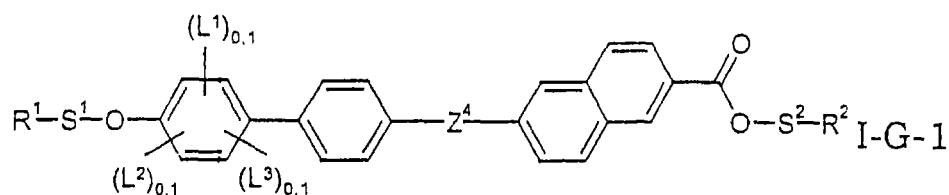
10 L¹, L², L³ each independently of the others represents hydrogen,
C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₂₀-alkoxy or
C₂-C₂₀-alkenyloxy, wherein at least one substituent must be
other than hydrogen;

Z⁴ represents -C≡C-, -COO- or -CH=CH-COO-;

15 Z⁵ represents a single bond, -COO- or -CH=CH-COO-; and

R¹, R², S¹ and S²
are as defined in claim 1.

10. A compound according to any one of claims 1 to 5 of formula I-G-1



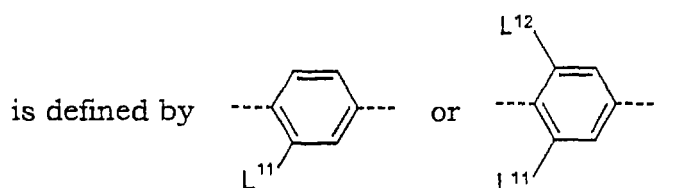
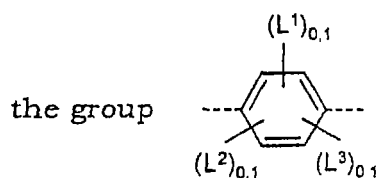
wherein

L^1, L^2, L^3 each independently of the others represents hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy or C_2 - C_{20} -alkenyloxy, wherein at least one substituent must be other than hydrogen;

Z^4 represents $-C\equiv C-$, $-COO-$, $-CH=CH-COO-$; and

R^1, R^2, S^1 and S^2 are as defined in claim 1.

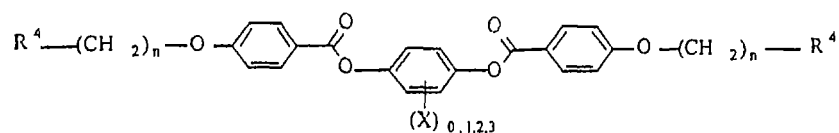
11. A compound according to any one of claims 6 to 10, in which



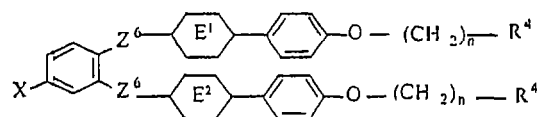
wherein L^{11}, L^{12} each independently of the other represents C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy or C_2 - C_{20} -alkenyloxy.

12. A crosslinkable liquid crystalline mixtures consisting of at least two components, of which at least one component is a compound according to any one of claims 1 to 11.

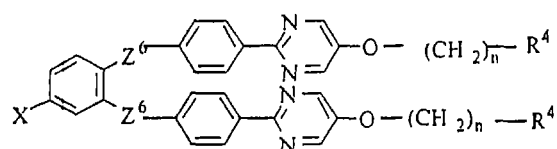
13. A crosslinkable liquid crystalline mixtures according to claim 12, characterised in that they comprise, in addition to one or more compounds according to one or more of claims 1 to 11, one or more compounds from the group of formulae



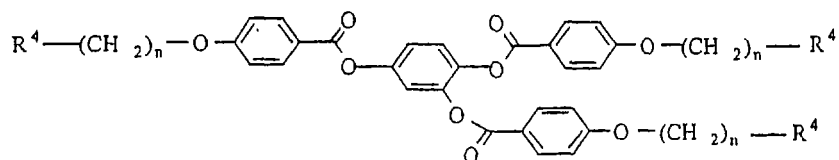
II



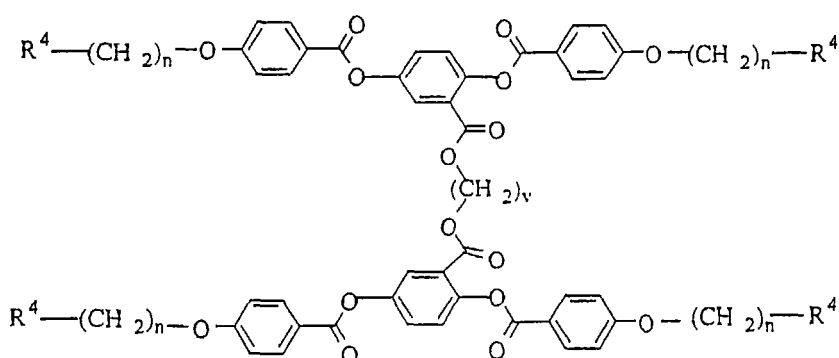
III



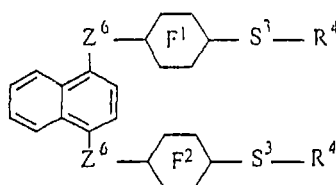
IV



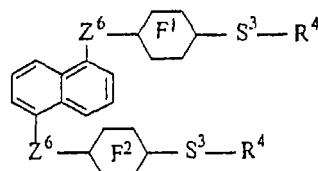
V



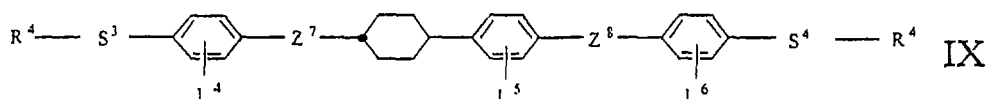
VI



VII



VIII



IX

wherein

- 5 R^4 represents a polymerisable group;
- S^3, S^4 each independently of the other is $-(CH_2)_n-$ or $-O(CH_2)_n-$;
- E^1, E^2 each independently of the other represents 1,4-phenylene, *trans*-1,4-cyclohexylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl or *trans*-1,4-cyclohexylene-1,4-phenylene;
- 10 F^1, F^2 each independently of the other represents 1,4-phenylene or 2- or 3-fluoro-1,4-phenylene;
- L^4, L^5, L^6 each independently of the others represents hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy, C_1 - C_{20} -alkoxy-carbonyl, formyl, C_1 - C_{20} -alkylcarbonyl, C_1 - C_{20} -alkylcarbonyloxy, halogen, cyano or nitro;
- 15 each Z^6 independently of any other represents $-COO-$, $-OOC-$, $-OCH_2-$, $-CH_2O-$, $-O(CH_2)_3-$, $-OOC(CH_2)_2-$ or $-COO(CH_2)_3-$;
- Z^7 represents a single bond, $-CH_2CH_2-$, $-CH_2O-$, $-OCH_2-$,

-COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃-, -(CH₂)₃O- or -C≡C- ;

Z⁸ represents a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-,
-COO-, -OOC- or -C≡C- ;

5 each X independently of any other(s) represents hydrogen,
C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₂₀-alkoxy,
C₁-C₂₀-alkoxycarbonyl, formyl, C₁-C₂₀-alkylcarbonyl,
C₁-C₂₀-alkylcarbonyloxy, fluorine, chlorine, bromine, cyano
or nitro;

10 each n independently of any other(s) is an integer from 2 to 20; and
v is an integer from 2 to 12.

14. A crosslinkable liquid crystalline mixtures according to claim 13,
wherein

15 R⁴ represents a polymerisable group comprising CH₂=CH-,
CH₂=CH-O-, CH₂=CH-COO-, CH₂=C(CH₃)-COO-,
CH₂=C(Cl)-COO- or $\text{H}_2\text{C} \begin{array}{c} \diagup \text{CH-} \\ \diagdown \text{O} \end{array}$.

15. An optical or electro-optical device comprising a compound according
to any one of claims 1 to 11.

16. An optical or electro-optical device comprising a crosslinkable liquid
crystalline mixture according to any one of claims 12 to 14.

20 17. Use of a compound according to any one of claims 1 to 11 in its
crosslinked state for an optical or electro-optical device.

18. Use of a crosslinkable liquid crystalline mixture according any one of

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claims 12 to 14 in its crosslinked state for an optical or electro-optical device.