

PHOTOPOLYMERIZABLE LIQUID CRYSTALS

The present invention is concerned with photochemically oligomerisable or polymerisable liquid crystals, liquid crystalline mixtures which contain such compounds as well as their use in the cross-linked state as optical or electronic components.

Liquid crystals having at least two photochemically oligomerisable or polymerisable groups can be orientated on a substrate or in a cell, for example by orientating layers or in a field. These orientated liquid crystals, provided with a suitable amount of a photoinitiator, are polymerised by irradiation with light of a suitable wavelength. The cross-linked structure which is thereby produced remains even at high temperatures. Such layers can be, for example, parts of hybrid layers as described in Swiss Patent Applications CH 2016/94 and CH 2017/94. Thus, optical components such as, for example, retarders, wave guides, optical grids and filters, integrated colour filters or cells with piezoelectric and with non-linear optical (NLO) properties, etc. can be prepared. Such optical components find use, for example, in projection systems.

Further properties such as, for example, the birefringence, the refractive index, the transparency, etc. must fulfil different requirements depending on the field of application. For example, networks for optical retarders should have a high birefringence in order that the layer thickness of the integrated optical component can be kept to a minimum.

Polymers which are electrically insulating, but which have a good thermal conductivity are used in microelectronics in order to rapidly and efficiently disperse heat which results when a high density of components is operated. There is also a need for insulating layers having a low dielectric constant and a high heat resistance. Homogeneously orientated liquid crystalline networks are advantageous for such applications by virtue of

their low thermal expansion coefficients, high thermal conductivity and stability.

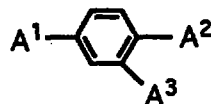
In addition to the general interest in photochemically oligomerisable or polymerisable liquid crystals for optical and electrical components, there is also a need for such compounds in other areas. Thus, such liquid crystalline materials are also suitable for cladding glass fibres for optical data transmission. The use of such networks increases the elastic modulus in the longitudinal axis of the fibre, lessens the thermal expansion coefficient and reduces microdistortion losses. This leads to an increased mechanical stability.

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. However, a spontaneous thermal polymerisation can occur prematurely in the processing, which is carried out at temperature barely below the clearing point, because at this temperature the viscosity in the liquid crystalline state is at its lowest and is therefore favourable for a good orientability. This spontaneous polymerisation leads to the formation of domains, whereby the optical and thermal properties in the cross-linked layers produced can be clearly influenced. The melting point can be decreased by producing complicated mixtures with several components, which indeed permits a processing at lower temperatures, but brings with it the danger of a crystallisation of conventional polymerisable liquid crystals.

There is accordingly the need to produce photochemically oligomerisable or polymerisable compounds which satisfy the aforementioned requirements. They should have low melting points and clearing points in order that they can be processed very readily at temperatures above room temperature in the liquid crystalline state and also in solution. Further, they should be orientable and structurable as domain-free as possible.

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

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



I

wherein

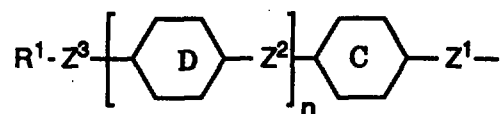
A¹, A², A³ signify photochemically oligomerisable or polymerisable mesogenic residues.

The mesogenic photochemically oligomerisable or polymerisable residues A¹, A² and A³ can be different or the same. Mesogenic residues will be known to a person skilled in the art and are described, for example, in "Flüssigkristalle in Tabellen" Vol. II, Deutscher Verlag für Grundstoffindustrie, Leipzig, 1984. These known mesogenic residues are provided terminally with a polymerisable residue in order that they are suitable for the above purpose.

The compounds of general formula I have a good solubility in usual solvents such as, for example, in anisole, N,N'-dimethylacetamide or N-methylpyrrolidone and are distinguished by a relatively low viscosity. They can therefore be applied to a suitable surface without problems. This usually takes place by spin-coating. Since, moreover, the compounds in accordance with the invention have a liquid crystalline phase, they can be directed, prior to the cross-linking, on an orientating layer or by applying an electric or magnetic field.

Preferred compounds of formula I are those in which the photochemically oligomerisable or polymerisable mesogenic

residues A¹, A² and A³ each independently signify residues of the formula



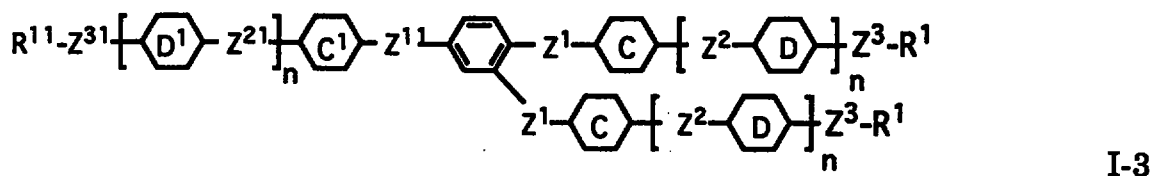
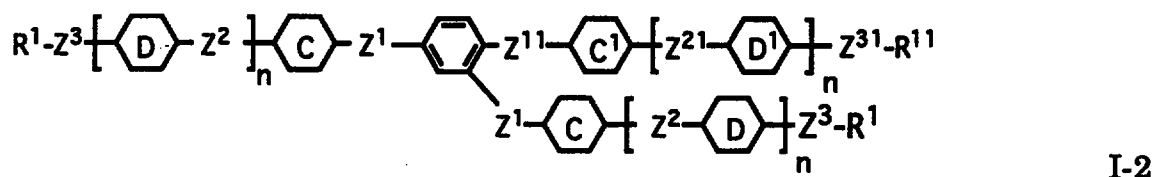
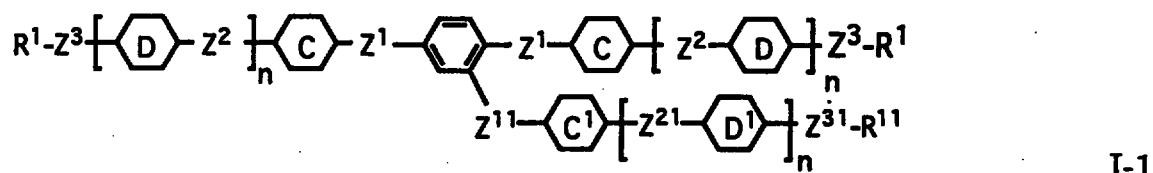
II

wherein

- C and D each independently signify 1,4-phenylene optionally substituted with nitro, acetyl, halogen, methyl and/or cyano, pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene or trans-1,3-dioxane-2,5-diyl;
- Z¹ signifies a single bond, -CH₂CH₂-, -CH₂O-, -COO-, -OOC-, -(CH₂)₄- or -(CH₂)₃O- ;
- Z² signifies a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;
- Z³ signifies -(CY₂)_m-, -(CY₂)_mO-, -(CY₂)_mCOO-, -(CY₂)_mOOC, -(Si[(CH₃)₂O]_p-, -OCH₂(Si[(CH₃)₂O]_pSi[(CH₃)₂]CH₂O- or -NHCH₂(Si[(CH₃)₂O]_pSi[(CH₃)₂]CH₂NH-;
- Y signifies hydrogen or fluorine;
- m signifies a whole number of 1 to 16;
- p signifies a whole number of 1 to 16;
- n signifies 0 or 1; and
- R¹ signifies a polymerisable group such as acrylate, allyl ether, allyl ester, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloyl-phenylene, acrylamide, methacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyl ether, vinyl ester, styrene derivative, maleic acid derivative, fumaric acid derivative or a dimerisable group such as, for example, chalcone or a cinnamic acid derivative optionally substituted with methyl, methoxy, cyano and/or halogen.

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

Compounds of formula I in which two of the mesogenic residues A^1 , A^2 and A^3 have the same significance are preferred. These are compounds of the formulae



wherein

C, C^1, D and D^1

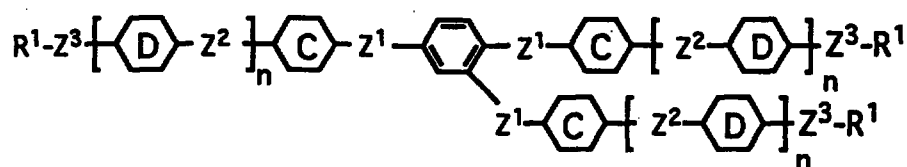
each independently signify 1,4-phenylene optionally substituted with nitro, acetyl, halogen, methyl and/or cyano, pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene or trans-1,3-dioxane-2,5-diyl;

Z^1 and Z^{11}

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

Z^2 and Z^{21}	each independently signify a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{OCH}_2-$, $-\text{COO}-$, $-\text{OOC}-$, $-(\text{CH}_2)_4-$, $-\text{O}(\text{CH}_2)_3-$ or $-(\text{CH}_2)_3\text{O}-$;
Z^3 and Z^{31}	each independently signify $-(\text{CY}_2)_m-$, $-(\text{CY}_2)_m\text{O}-$, $-(\text{CY}_2)_m\text{COO}-$, $-(\text{CY}_2)_m\text{OOC}-$, $-(\text{Si}[(\text{CH}_3)_2]\text{O})_p-$, $-\text{OCH}_2(\text{Si}[(\text{CH}_3)_2]\text{O})_p\text{Si}[(\text{CH}_3)_2]\text{CH}_2\text{O}-$ or $-\text{NHCH}_2(\text{Si}[(\text{CH}_3)_2]\text{O})_p\text{Si}[(\text{CH}_3)_2]\text{CH}_2\text{NH}-$;
Y	signifies hydrogen or fluorine;
m	signifies a whole number of 1 to 16;
p	signifies a whole number of 1 to 16;
n	signifies 0 or 1; and
R^1 and R^{11}	each independently signify a polymerizable group such as acrylate, allyl ether, allyl ester, methacrylate, 2-chloro-acrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-phenyl-acrylamide, epoxy, itaconic acid ester, vinyl ether, vinyl ester, styrene derivative, maleic acid derivative, fumaric acid derivative or a dimerisable group such as, for example, chalcone or a cinnamic acid derivative optionally substituted with methyl, methoxy, cyano and/or halogen.

Quite particularly preferred compounds of formula I are those in which the mesogenic residues A^1 , A^2 and A^3 are the same, i.e. compounds of the formula



I-4

wherein the symbols have the aforementioned significances.

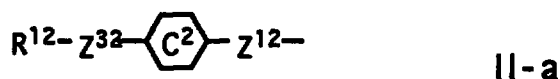
The mesophase type of the compounds in accordance with the invention can be influenced by varying the rings C or C^1 and D or D^1 . Thus, heterocyclic rings have the tendency to produce

smectic phases, while phenylene and cyclohexylene rings promote nematic tendencies. Preferably, rings C or C¹ and D or D¹ each independently signify 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, pyridine-2,5-diyl or pyrimidine-2,5-diyl, especially 1,4-phenylene, 2-fluoro-1,4-phenylene or 3-fluoro-1,4-phenylene.

Especially preferred compounds of formulae I-1 to I-4 are compounds in which Z¹ and, respectively, Z¹¹ signify -CH₂O-, -COO- or -OOC-; Z² and, respectively, Z²¹ signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO- or -OOC- and Y signifies hydrogen.

In especially preferred compounds of formulae I-1 to I-4 the residues R¹ and, respectively, R¹¹ signify acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-phenylacrylamide, epoxy, vinyl ether, vinyl ester, styrene derivative, maleic acid derivative or fumaric acid derivative and the like; acrylate, methacrylate, vinylether and epoxy are quite especially preferred.

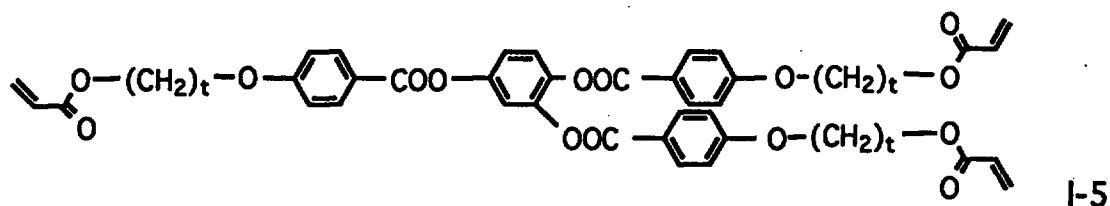
The mesogenic residues A¹, A² and A³ preferably signify a residue of formula II in which n = 0 such as, for example



wherein

- | | |
|-----------------|--|
| R ¹² | signifies acrylate, methacrylate or epoxy; |
| Z ³² | signifies -(CH ₂) _t -, -(CH ₂) _t O-, -(CH ₂) _t COO- or -(CH ₂) _t OOC-; |
| t | signifies a whole number of 3 to 12; |
| C ² | signifies 1,4-phenylene, 2-fluoro-1,4-phenylene or 3-fluoro-1,4-phenylene; and |
| Z ¹² | signifies -CH ₂ O-, -COO- or -OOC-. |

The compounds of the formula



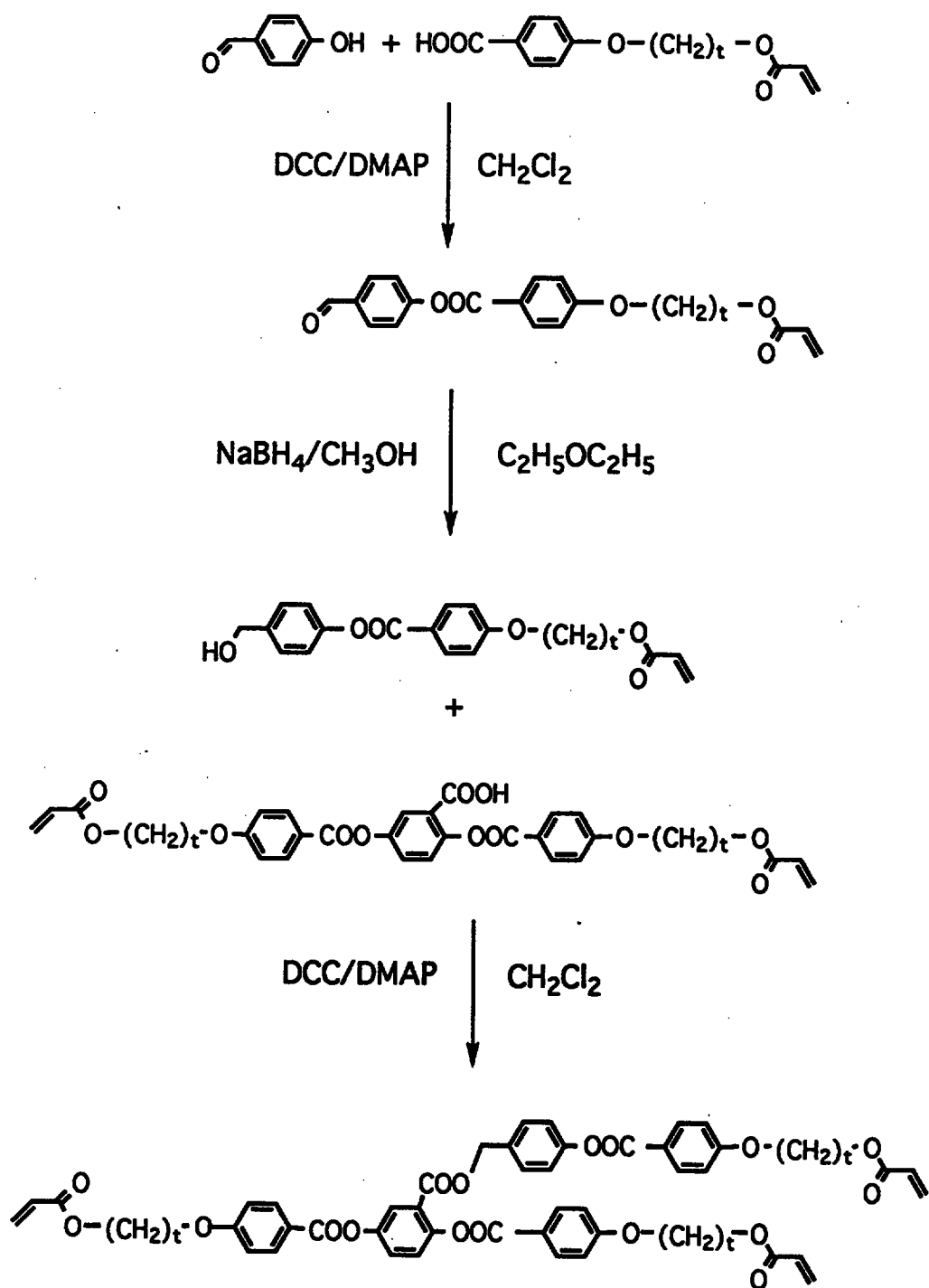
wherein t signifies a whole number of 3 to 12, are quite especially preferred.

The compounds of general formulae I, I-1, I-2 and I-3 in accordance with the invention in which the mesogenic residues A^1 , A^2 and A^3 are different from one another are very readily accessible synthetically and can be produced in a manner known per se, for example analogously to the methods illustrated in Schemes 1 to 3 as well as in the Examples.

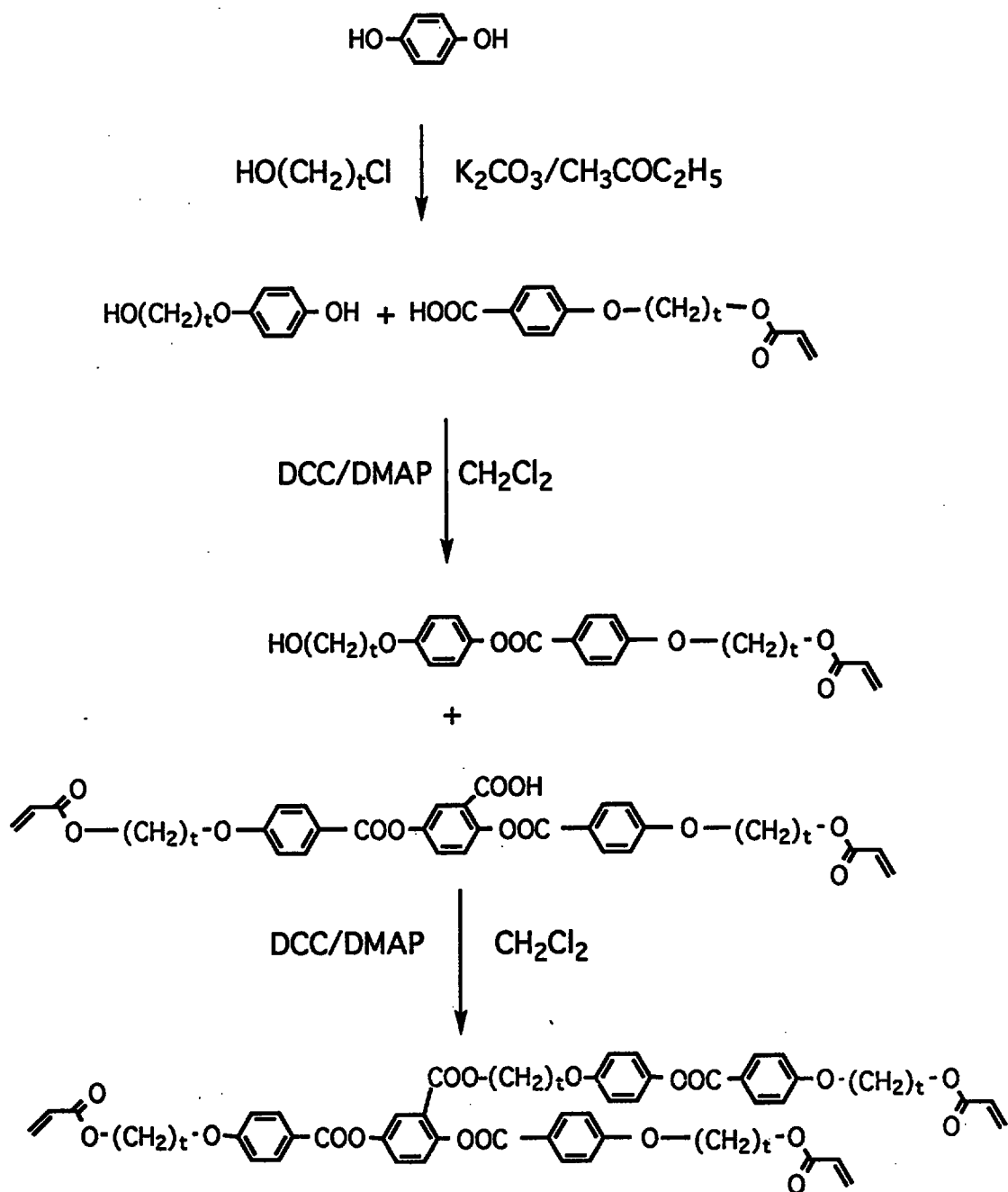
The mesogenic residues of formulae II and II-a are known or are analogues of known structures and can be prepared in a manner known per se and subsequently linked with the aromatics.

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

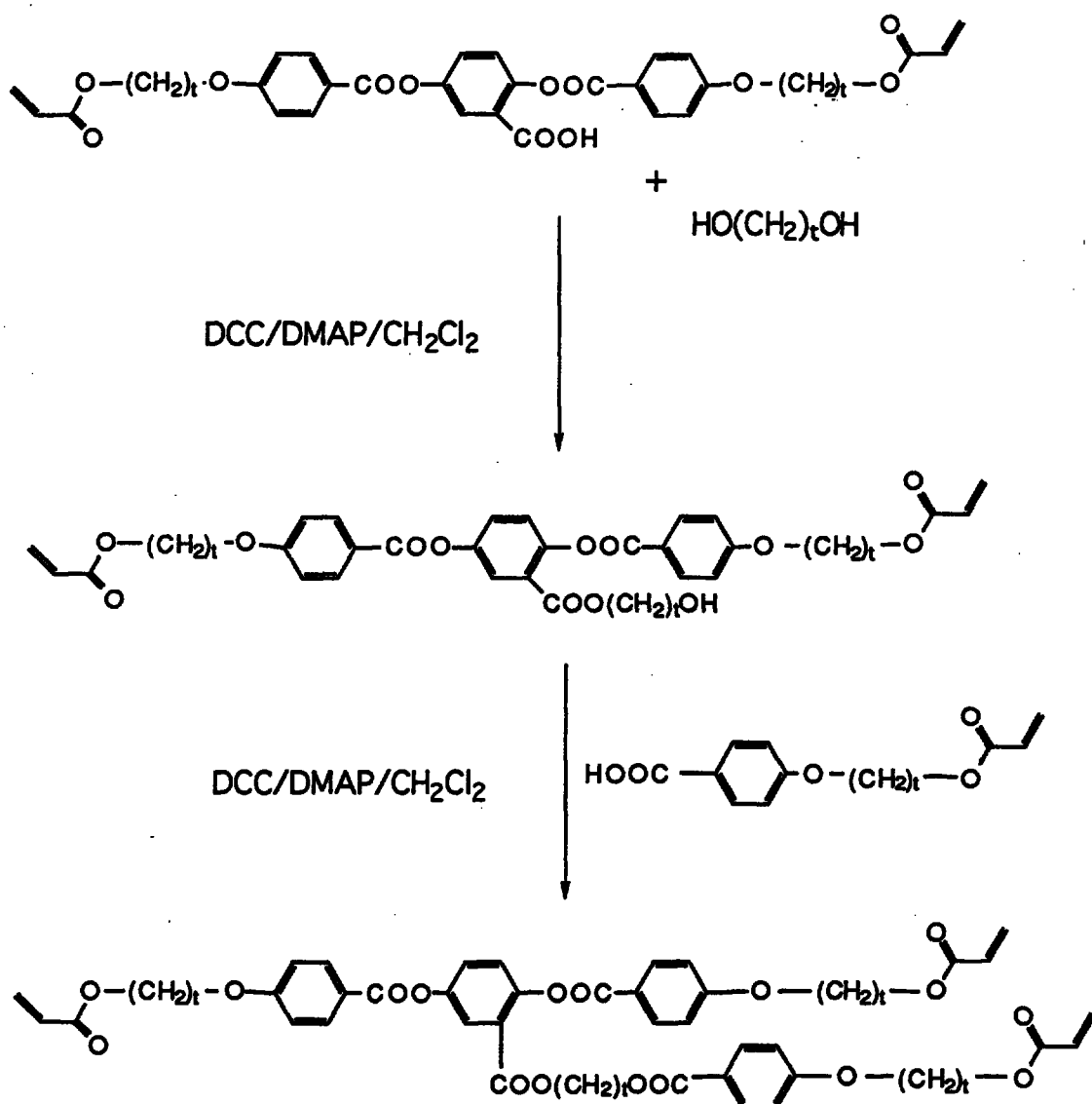
Scheme 1



Scheme 2



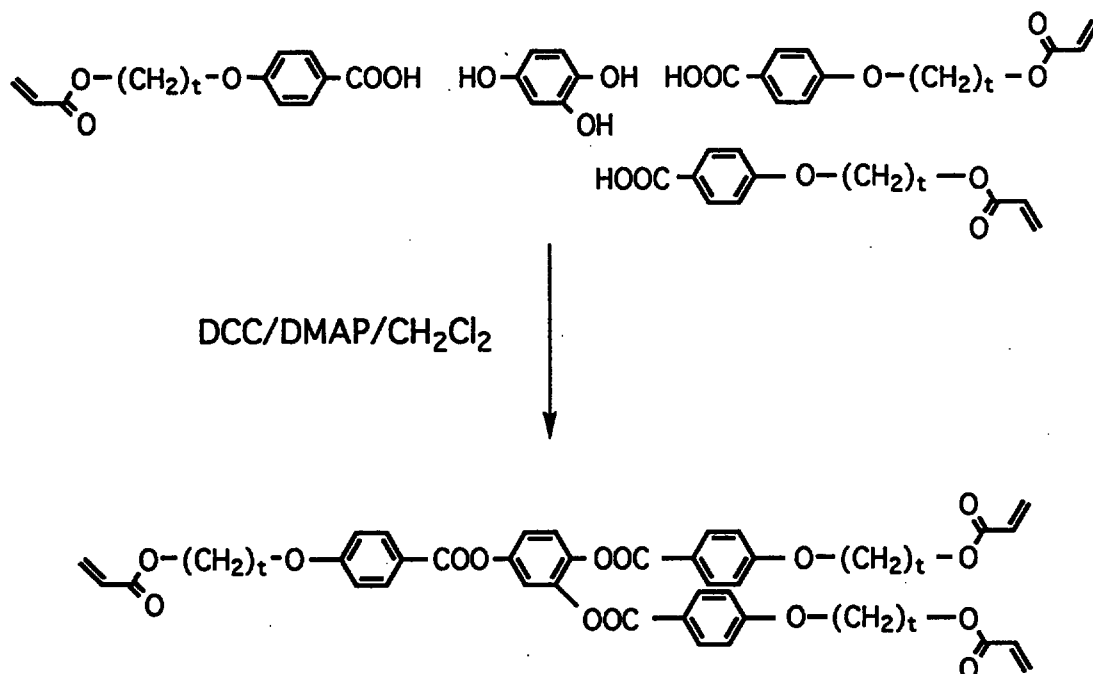
Scheme 3



Compounds of formulae I-4 and I-5 in which the mesogenic residues A^1 , A^2 and A^3 are the same can be produced, for example, in a manner which is simple and known per se from 1,2,4-trihydroxyphenol and the corresponding acid derivatives of formula II such as 4-[n-acryloyloxyalkoxy]benzoic acids as shown in Scheme 4. The esterification can be effected, for example, in the presence of N,N'-dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine in dichloromethane or another suitable solvent such as e.g. chloroform.

The starting materials are known and are to some extent commercially available.

Scheme 4

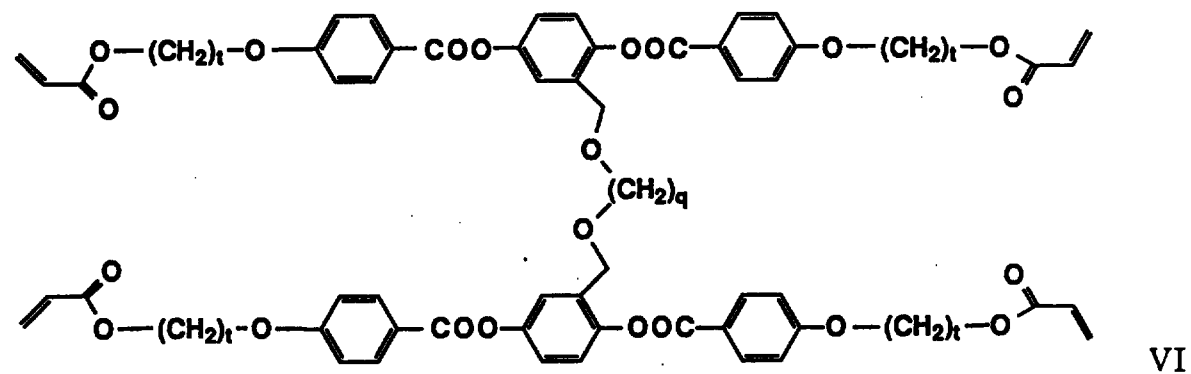
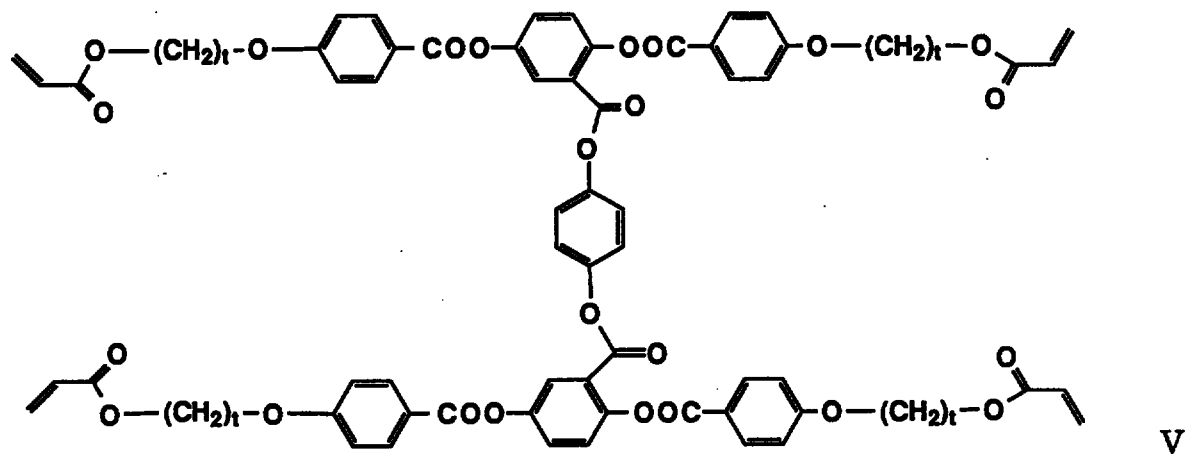
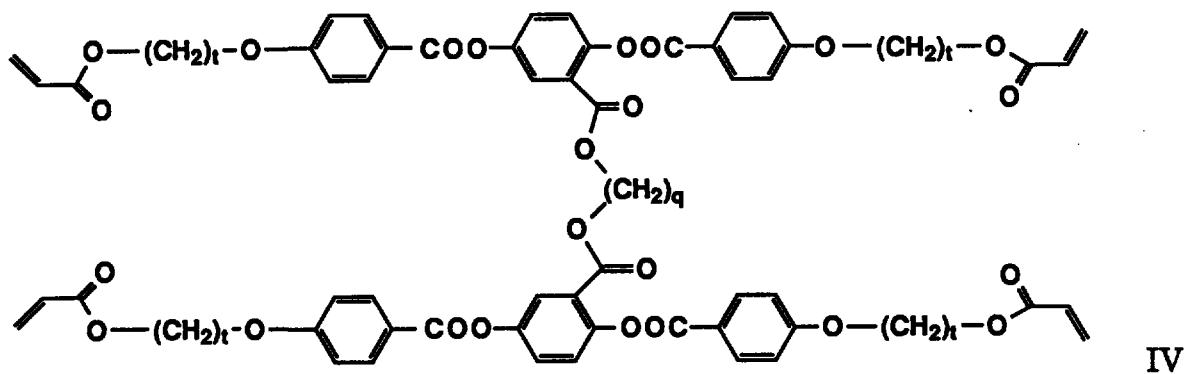
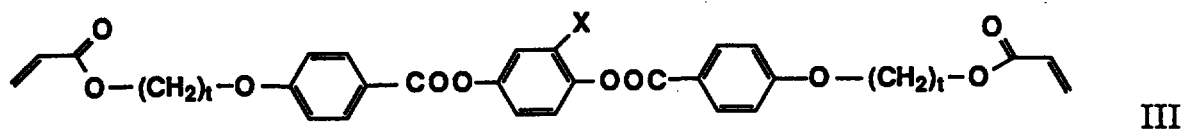


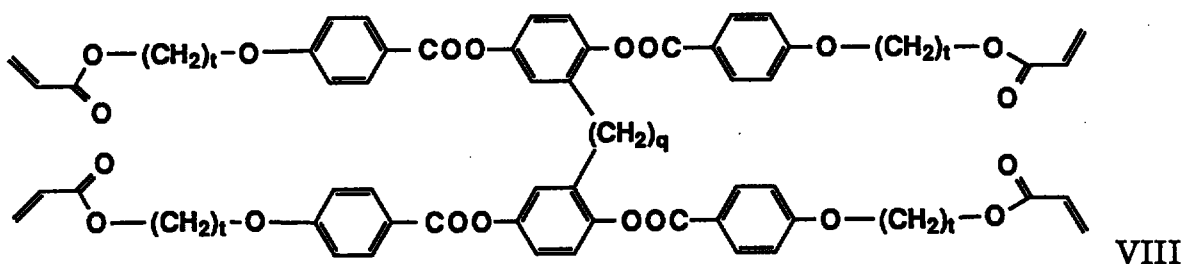
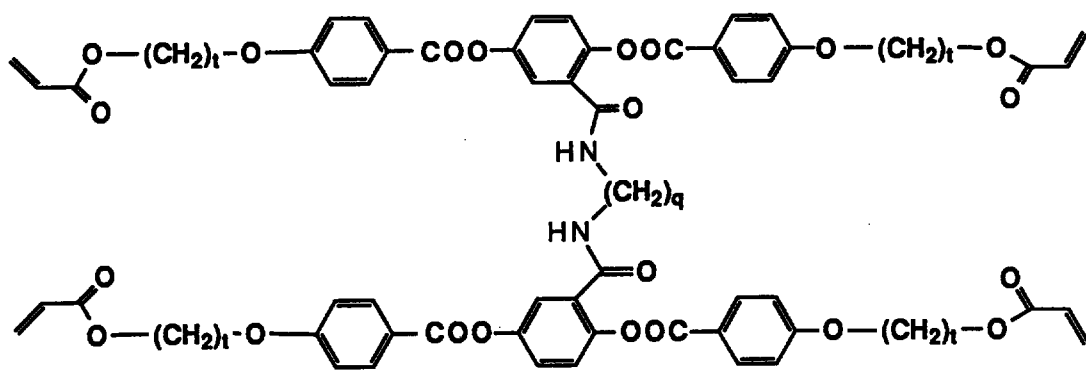
The compounds of formulae I can be used as single compounds or in the form of mixtures with one another and/or with other liquid crystal components.

The liquid crystalline mixtures in accordance with the invention contain at least two components, of which at least one component is a compound of formula I. A second component and any other components can be additional compounds of formula I or other known liquid crystal compounds with or without photo-cross-linkable groups. Also, one or more chiral compounds can be present in the mixture.

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

compounds of formula I, one or more compounds from the group of compounds of the general formulae





wherein

t q X	signifies a whole number of 3 to 12; signifies a whole number of 2 to 12; and signifies hydrogen, fluorine, chlorine or lower alkyl such as methyl, ethyl, propyl or butyl.
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The production of the compounds of formula I and of liquid crystalline mixtures containing these compounds are illustrated in more detail by the following Examples. C signifies a crystalline phase, S signifies a smectic phase, N signifies a nematic phase and I signifies the isotropic phase.

Example 1

5.0 g of N,N'-dicyclohexylcarbodiimide were added at room temperature while stirring to a solution of 4.7 g of 4-[6-acryloyloxyhexyloxy]benzoic acid, 0.5 g of trihydroxybenzene and 0.2 g of 4-dimethylaminopyridine in 25 ml of dichloromethane. The reaction mixture was stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of dichloromethane each time. The combined organic

phases were washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate was subsequently concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl acetate (vol. 3:1) and two-fold recrystallization from ethyl alcohol of the fractions which were pure according to thin-layer chromatography gave 2.0 g of 1,2,4-tri(4-[6-acryloyloxyhexyloxy]-phenylcarbonyloxy)-benzene; m.p. (C-I) 44°C, cl.p. (N-I) 33°C.

The following compounds were prepared in an analogous manner:

1,2,4-Tri(4-[3-acryloyloxypropyloxy]phenylcarbonyloxy)benzene;
 1,2,4-tri(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)benzene;
 m.p. (C-I) 46°C, cl.p. (N-I) -8°C;
 1,2,4-tri(4-[5-acryloyloxypentyloxy]phenylcarbonyloxy)benzene;
 m.p. (C-I) 39°C, cl.p. (N-I) 33°C;
 1,2,4-tri(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)benzene;
 m.p. (C-N) 31°C, cl.p. (N-I) 44°C;
 1,2,4-tri(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzene;
 m.p. (C-I) 56°C, cl.p. (N-I) 42°C;
 1,2,4-tri(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)benzene;
 m.p. (C-N) 41°C, cl.p. (N-I) 51°C;
 1,2,4-tri(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)benzene;
 m.p. (C-I) 55°C; cl.p. (N-I) 46°C;
 1,2,4-tri(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-
 benzene; m.p. (C-N) 44°C; cl.p. (N-I) 53°C.

Example 2

0.2 g of N,N'-dicyclohexylcarbodiimide is added at room temperature while stirring to a solution of 0.6 g of 2,5-bis(4-[6-acryloyloxyhexyloxy]-phenylcarbonyloxy)-benzoic acid, 0.4 g [4-(4-[6-acryloyloxyhexyloxy]-phenylcarbonyloxy)phenyl]methanol and 0.04 g of 4-dimethylaminopyridine in 20 ml of dichloromethane. The reaction mixture is stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of dichloromethane 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 subsequently concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl acetate (vol. 1:1) and two-fold recrystallization from acetone of the fractions which are pure according to thin-layer chromatography gives 0.4 g of [4-(4-[6-acryloyloxyhexyloxy]-phenylcarbonyloxy)-phenyl]-methyl 2,5-bis(4-[6-acryloyloxyhexyloxy]-phenylcarbonyloxy)-benzoate.

The [4-(4-[6-acryloyloxyhexyloxy]-phenylcarbonyloxy)-phenyl]-methanol used as the starting material is prepared as follows:

(a) A mixture of 0.13 g of sodium borohydride and 15 ml of water is treated dropwise at 0°C with a solution of 0.8 g of 4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)benzaldehyde in 100 ml of dioxan. The reaction mixture is stirred at 0°C for a further 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 time. The combined aqueous phases are extracted twice with 50 ml of dichloromethane each time. The combined organic phases are then washed twice with 100 ml of water each time, dried over magnesium sulphate, the suspension is filtered and the filtrate is concentrated. The residue is used in the next step without further purification.

(b) 0.6 g of N,N'-dicyclodicyclohexylcarbodiimide is added at room temperature while stirring to a solution of 1.0 g of 4-[6-acryloyloxyhexyloxy]benzoic acid, 0.3 g of 4-hydroxybenzaldehyde and 0.04 g of 4-dimethylaminopyridine in 20 ml of dichloromethane. The reaction mixture is stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of dichloromethane 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 subsequently concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl

acetate (vol. 1:1) and two-fold recrystallization from ethanol of the fractions which are pure according to thin-layer chromatography gives 0.9 g of 4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)benzaldehyde.

The following compounds can be prepared in an analogous manner:

[4-(4-[6-Acryloyloxyhexyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[3-acryloyloxypropyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[5-acryloyloxyptyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)phenyl]-methyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-phenyl]methyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;

[4-(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-phenyl]methyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)benzoate.

Example 3

0.6 g of 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-benzoic acid, 0.4 g of [4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenoxy]ethanol, 0.04 g of 4-dimethylaminopyridine and 0.2 g of N,N'-dicyclodicyclohexylcarbodiimide in 20 ml of dichloromethane are reacted in an analogous manner to Example 1 to give [4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenoxy]ethyl 2,5-bis(4-[6-acryloyloxyhexyloxy])phenylcarbonyloxy)benzoate.

The [4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-phenoxy]ethanol used as the starting material is prepared as follows:

(a) 0.6 g of 4-[6-acryloyloxyhexyloxy]benzoic acid, 0.2 g of (4-hydroxyphenoxy)ethanol, 0.04 g of 4-dimethylaminopyridine and 0.4 g of N,N'-dicyclodicyclohexylcarbodiimide in 50 ml of dichloromethane are reacted in an analogous manner to Example 1 to give 0.4 g of [4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]ethanol.

The following compounds can be prepared in an analogous manner:

[4-(4-[6-Acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[3-acryloyloxypropyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[5-acryloyloxyptyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-ethyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-propyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-butyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)-benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-
pentyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)-
benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-
hexyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-
benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-
heptyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-
benzoate;

[4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)phenoxy]-
octyl 2,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-
benzoate.

Example 4

0.3 g of 4-[6-acryloyloxyhexyloxy]benzoic acid, 0.8 g of 4-
hydroxybutyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenyl-
carbonyloxy)benzoate, 0.04 g of 4-dimethylaminopyridine and
0.2 g of N,N'-dicyclodicyclohexylcarbodiimide in 50 ml of
dichloromethane are reacted in an analogous manner to Example 1
to give 0.5 g of 4-(4-[6-acryloyloxyhexyloxy]phenylcarbonyl-
oxy)butyl 2,5-bis(4-[11-acryloyloxyundecyloxy])phenylcarbonyl-
oxy)benzoate.

The following compounds can be prepared in an analogous
manner:

3-(4-[6-Acryloyloxyhexyloxy]phenylcarbonyloxy)propyl 2,5-
bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;

5-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)pentyl 2,5-
bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;

6-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)hexyl 2,5-
bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;

7-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)heptyl 2,5-
bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;

8-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)octyl 2,5-
bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;

9-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)nonyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;
 10-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)decyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;
 11-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)undecyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;
 12-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)dodecyl 2,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)benzoate;
 3-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)propyl 2,5-bis(4-[5-acryloyloxypropyloxy]phenylcarbonyloxy)benzoate;
 3-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)propyl 2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)benzoate;
 3-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)propyl 2,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)benzoate;
 3-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)propyl 2,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)benzoate;
 3-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)propyl 2,5-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)benzoate;
 3-(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)propyl 2,5-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)benzoate.

Example 5

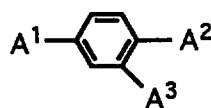
A mixture (C-N, <20°C, N-I, 38°C) of 80 wt.% 1,2,4-tri(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)benzene and 20 wt.% 1-chloro-2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-benzene was treated with 1 wt.% of a photoinitiator (IRGACURE, Ciba Geigy), dissolved in anisole (40 wt.%) and then spun at 2000 revolutions per minute on to a glass plate. The glass plate had previously been coated with methacryloyloxyethyl 3-(E)-[4-cyano-4'-biphenyl]acrylate and then irradiated with linear polarised light. Thereby, a predetermined structure was inscribed photolithographically by means of a mask in the (PPN) layer. The spun-on new layer (on the PPN layer) was dried at 90°C on a heating block, then irradiated with xenon light in a vacuum oven under a vacuum at 90°C. The inscribed original structure

remained and was copied faithfully by the new network. A clear double refraction (Δn) was recognizable. This layer functions as a structural optical retarder.



Claims

1. Compounds of the general formula

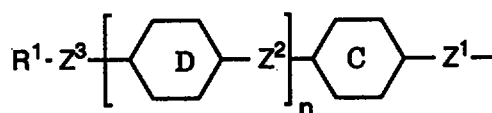


I

wherein

A¹, A², A³ signify photochemically oligomerisable or polymerisable mesogenic residues.

2. Compounds according to claim 1, wherein the mesogenic residues A¹, A² and A³ each independently signify residues of the formula



II

wherein

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

Z¹ signifies a single bond, -CH₂CH₂-, -CH₂O-, -COO-, -OOC-, -(CH₂)₄- or -(CH₂)₃O-;

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

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

Y signifies hydrogen or fluorine;

m signifies a whole number of 1 to 16;

p signifies a whole number of 1 to 16;

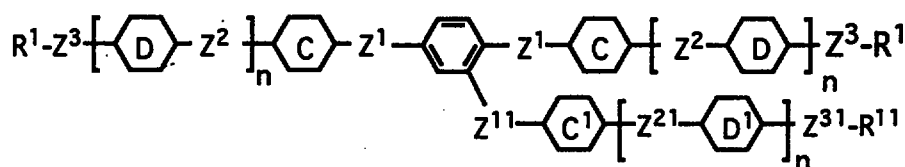
n signifies 0 or 1; and



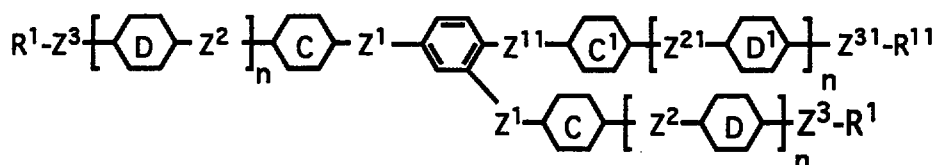
R^1 signifies a polymerisable group such as acrylate, allyl ether, allyl ester, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloyl-phenylene, acrylamide, methacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyl ether, vinyl ester, styrene derivative, maleic acid derivative, fumaric acid derivative or a dimerisable group such as, for example, chalcone or a cinnamic acid derivative optionally substituted with methyl, methoxy, cyano and/or halogen.

3. Compounds according to claim 1 or 2, wherein two of the mesogenic residues A^1 , A^2 and A^3 have the same significance.

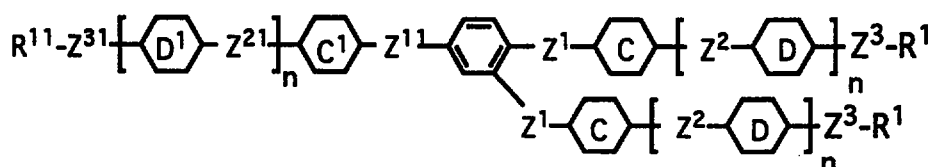
4. Compounds according to any one of claims 1 to 3 of the formulae



I-1



I-2



I-3

wherein

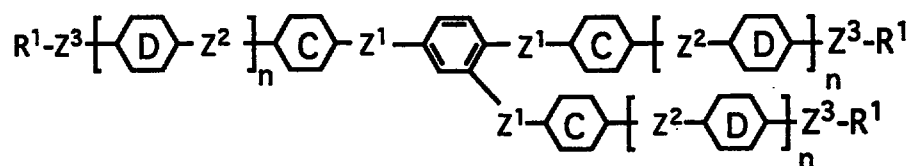
C, C^1, D and D^1

each independently signify 1,4-phenylene optionally substituted with nitro, acetyl, halogen, methyl and/or cyano, pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-



	cyclohexylene or trans-1,3-dioxane-2,5-diyl;
Z ¹ and Z ¹¹	each independently signify a single bond, -CH ₂ CH ₂ -, -CH ₂ O-, -COO-, -OOC-, -(CH ₂) ₄ - or -(CH ₂) ₃ O-;
Z ² and Z ²¹	each independently 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-;
Z ³ and Z ³¹	each independently signify -(CY ₂) _m -, -(CY ₂) _m O-, -(CY ₂) _m COO-, -(CY ₂) _m OOC, -(Si[(CH ₃) ₂]O) _p -, -OCH ₂ (Si[(CH ₃) ₂]O) _p Si[(CH ₃) ₂]CH ₂ O- or -NHCH ₂ (Si[(CH ₃) ₂]O) _p Si[(CH ₃) ₂]CH ₂ NH-;
Y	signifies hydrogen or fluorine;
m	signifies a whole number of 1 to 16;
p	signifies a whole number of 1 to 16;
n	signifies 0 or 1; and
R ¹ and R ¹¹	each independently signify a polymerizable group such as acrylate, allyl ether, allyl ester, methacrylate, 2-chloro-acrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyl ether, vinyl ester, styrene derivative, maleic acid derivative, fumaric acid derivative or a dimerisable group such as, for example, chalcone or a cinnamic acid derivative optionally substituted with methyl, methoxy, cyano and/or halogen.

5. Compounds according to claim 1 or 2 of the formula



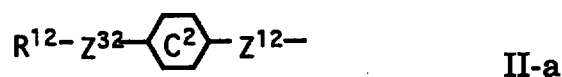
wherein the symbols have the significances given in claim 2.



6. Compounds according to claim 2 to 5, wherein Z^1 and, respectively, Z^{11} signify $-\text{CH}_2\text{O}-$, $-\text{COO}-$ or $-\text{OOC}-$; Z^2 and, respectively, Z^{21} signify a single bond, $-\text{CH}_2\text{CH}_2$, $-\text{CH}_2\text{O}-$, $-\text{OCH}_2-$, $-\text{COO}-$ or $-\text{OOC}-$; and Y signifies hydrogen.

7. Compounds according to claim 6, wherein R^1 and, respectively, R^{11} signifies acrylate, methacrylate, vinyl ether or epoxy.

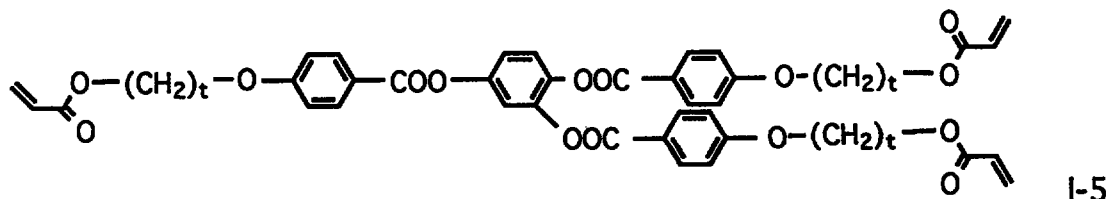
8. Compounds according to claim 1, wherein the mesogenic residues A^1 , A^2 and A^3 signify a residue of the formula



wherein

- R^{12} signifies acrylate, methacrylate or epoxy;
 Z^{32} signifies $-(\text{CH}_2)_t-$, $-(\text{CH}_2)_t\text{O}-$, $-(\text{CH}_2)_t\text{COO}-$ or $-(\text{CH}_2)_t\text{OOC}-$;
 t signifies a whole number of 3 to 12;
 C^2 signifies 1,4-phenylene, 2-fluoro-1,4-phenylene or 3-fluoro-1,4-phenylene; and
 Z^{12} signifies $\text{CH}_2\text{O}-$, $-\text{COO}-$ or $-\text{OOC}-$.

9. Compounds according to any one of claims 1, 2 and 5 to 8 of the formula

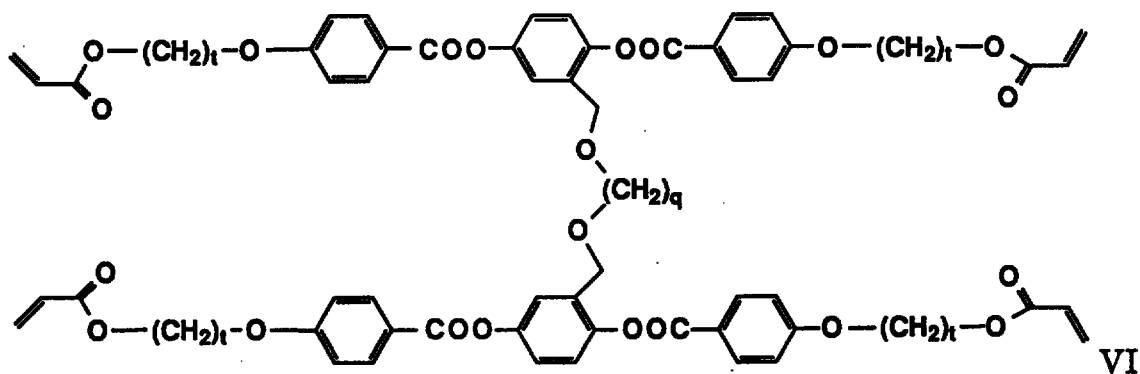
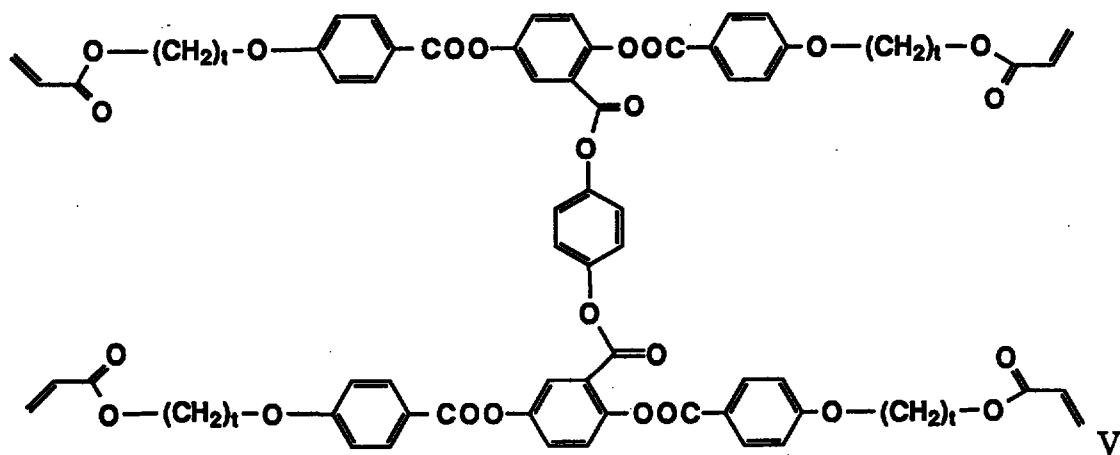
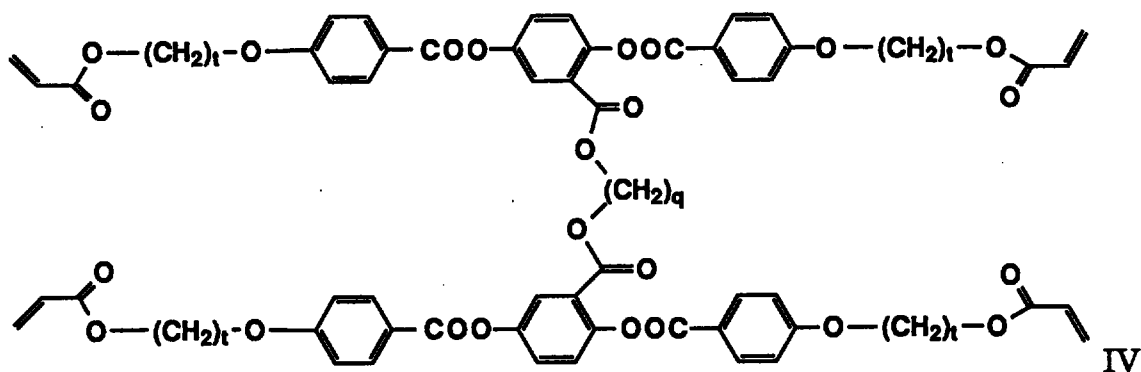
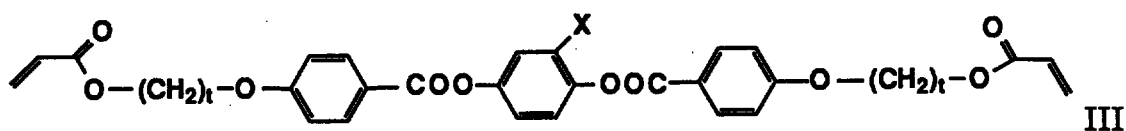


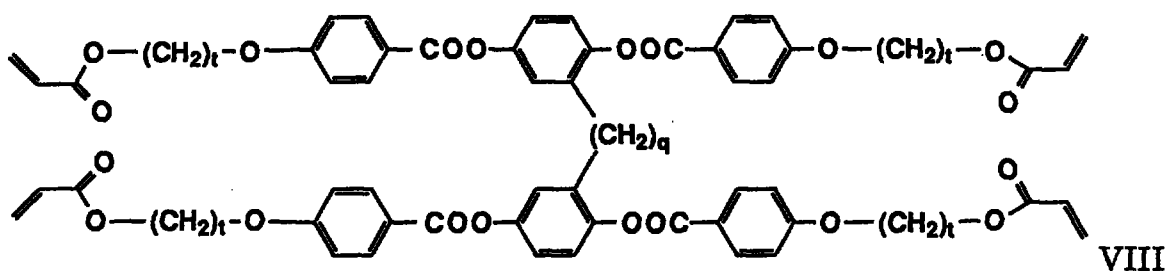
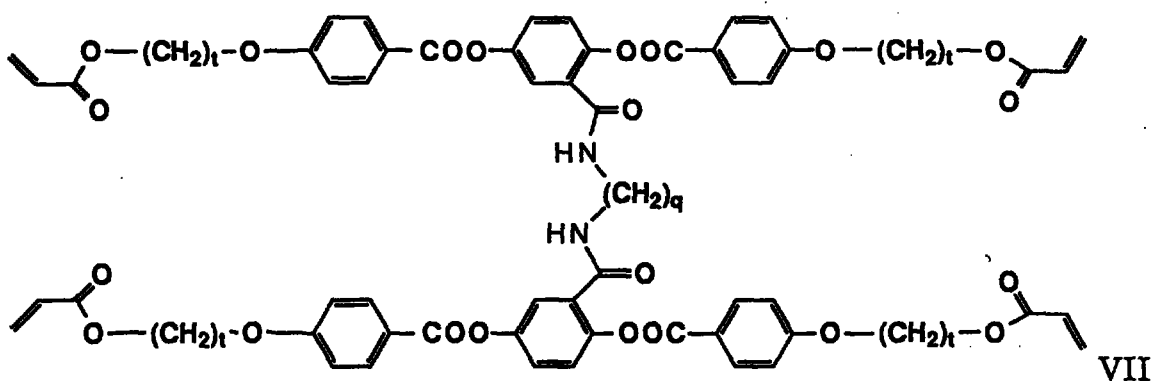
wherein t signifies a whole number of 3 to 12.

10. A polymerisable, liquid crystalline mixture consisting of at least two components, of which at least one component is a compound of formula I defined in claim 1.



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





wherein

t signifies a whole number of 3 to 12;
 q signifies a whole number of 2 to 12; and
 X signifies hydrogen, lower alkyl, fluorine or chlorine.

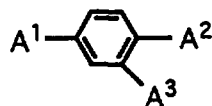
12. The use of compounds according to any one of claims 1 to 9 in their cross-linked state for optical components.

13. The use of photochemically oligomerisable or polymerisable, liquid crystalline mixtures according to claim 10 or 11 in their cross-linked state for optical or electronic components.

PHOTOPOLYMERIZABLE LIQUID CRYSTALS

Abstract

The present invention is concerned with photochemically oligomerisable or polymerisable liquid crystals of the general formula



I

wherein

A¹, A², A³

signify photochemically oligomerisable or polymerisable mesogenic residues,

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

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