

The present invention is concerned with photo cross-linkable naphthyl derivatives, mixtures which contain such compounds and their use in the cross-linked state for optical 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 thereby produced remains even at high temperatures. Such layers can be, for example, parts of hybrid layers, as are described in Swiss Patent Applications CH 2016/94 and CH 2017/94. Thus, optical components such as, for example, retarders, wave guides, optical grids and filters, integrated colour filters or cells having piezoelectric properties and those having non-linear optical (NLO) properties, etc., can be produced. Such optical components are used, 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 use. For example, materials for optical retarders should have a high birefringence in order that the layer thickness of the integrated optical component can be held at a minimum.

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, reduces the thermal expansion coefficient and avoids microdistortion losses. This leads to an increased mechanical stability.



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

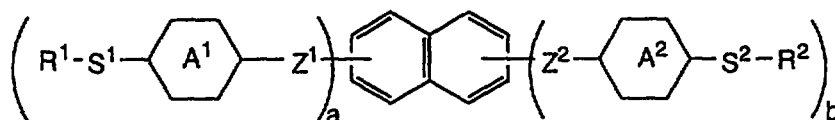
10 Since liquid crystals are usually used as mixtures of several components, it is important that the components have a good miscibility with one another. Conventional photochemically oligomerisable or polymerisable liquid crystals usually have a high melting point and clearing point. This has the disadvantage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

30 There is accordingly the need, especially for use in optical filters, to produce photochemically oligomerisable or polymerisable compounds which are distinguished by an especially high optical anisotropy and which at the same time have low melting points and clearing points in order that they can be
35 processed very readily at temperatures above room temperature in the liquid crystalline state and also in solution. Further, they should be orientable and structurable as domain-free as possible



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

The present invention now provides compounds which are
5 outstandingly suitable as single components or as components of liquid crystal mixtures for optical components, namely compounds of the general formula



10

wherein

R¹ and R²

15

each independently signify a cross-linkable group such as ethylene, acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyloxy, vinyl ester, styrene derivative, siloxane, ethyleneimine derivative, maleic acid derivative, fumaric acid derivative or a cinnamic acid derivative, which is optionally substituted with methyl, methoxy, cyano and/or halogen;

20

25

S¹ and S²

signify $-(CY_2)_m-$, $-O(CY_2)_m-$, $-(CY_2)_mO-$, $-(CY_2)_mCOO-$, $-(CY_2)_mOOC-$, $-(Si[(CH_3)_2]O)_m-$, $-OCH_2(Si[(CH_3)_2]O)_mSi[(CH_3)_2]CH_2O-$ or $-NHCH_2(Si[(CH_3)_2]O)_mSi[(CH_3)_2]CH_2NH-$;

30

Y

signifies hydrogen, fluorine or methyl;

a

signifies 0 or 1;

b

signifies 1 or 2, with the proviso that $a + b = 2$;

m

signifies a whole number of 1 to 16;

35

A¹ and A²

each independently signify 1,4-phenylene, which is optionally mono- or multiply-substituted with halogen, cyano, methyl,



- methoxy and/or acetyl, pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene or trans-1,3-dioxane-2,5-diyl; and
- 5 Z^1 and Z^2 each independently signify a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{OCH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{COO}-$, $-\text{OOC}-$, $-(\text{CH}_2)_4-$, $-\text{O}(\text{CH}_2)_3-$ or $-(\text{CH}_2)_3\text{O}-$.

10 The compounds of general formula I are distinguished by their relatively low viscosity. They can accordingly be applied without problems to a suitable surface. This generally 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 by the application of an

15 electric field.

 The term "1,4-phenylene, which is mono- or multiply-substituted with halogen, cyano, methyl, methoxy and/or acetyl," embraces in the scope of the present invention 1,4-phenylene,

20 1,4-phenylene substituted with fluorine, bromine, chlorine, cyano, methyl, methoxy or acetyl, such as, for example 2- or 3-fluoro-1,4-phenylene, 2,3-, 2,6- or 3,5-difluoro-1,4-phenylene, 2- or 3-chloro-1,4-phenylene, 2,3-, 2,6- or 3,5-dichloro-1,4-phenylene, 2- or 3-bromo-1,4-phenylene, 2- or 3-cyano-1,4-

25 phenylene, 2,3-dicyano-1,4-phenylene, 2- or 3-acetyl-1,4-phenylene, 2- or 3-methyl-1,4-phenylene, 2- or 3-methoxy-1,4-phenylene, and the like. Especially preferred compounds of formula I are those in which rings A^1 and A^2 are the same and signify 1,4-phenylene or 2- or 3-fluoro-1,4-phenylene.

30 The spacer groups S^1 and S^2 can also be chiral, if desired. Preferred compounds of formula I are those in which S^1 and S^2 have the same significance. Preferred spacer groups are those in which Y signifies hydrogen and m is a whole number of 4 to 12.

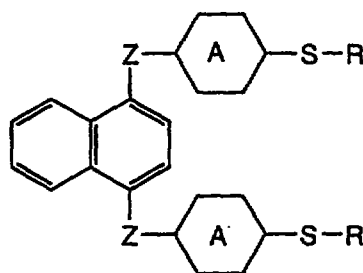
35 Preferred residues R^1 and R^2 are acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-phenylacrylamide, epoxy, vinyloxy, vinyl



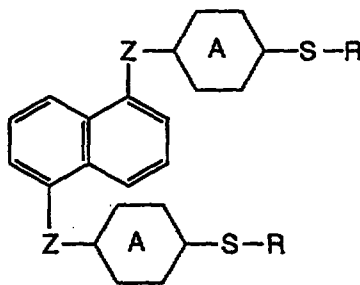
ester, styrene derivatives, maleic acid derivatives, fumaric acid derivatives and the like. It is these residues which can be cross-linked photochemically after coating the suitable carrier with compounds of formula I. In particular, there are preferred those compounds of formula I in which the residues R^1 and R^2 have the same significance. They preferably signify acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, vinyloxy or epoxy.

Especially preferred compounds of formula I are those in which the naphthyl ring is linked in position 1 and 5 or in position 1 and 4 with Z^1 and Z^2 , especially those in which Z^1 and Z^2 are the same and signify $-OCH_2-$, $-CH_2O-$, $-COO-$ or $-OOC-$.

Compounds which are quite especially preferred are those of the formulae



I-A



I-B

wherein

R signifies acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, vinyloxy or epoxy;

S signifies $-(CH_2)_{m'}-$, $-O(CH_2)_{m'}-$ or $-(CH_2)_{m'}O-$;

m' is a whole number of 4 to 12;

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- A signifies 1,4-phenylene or 2- or 3-fluoro-
1,4-phenylene; and
Z signifies -OCH₂- or -OOC-.

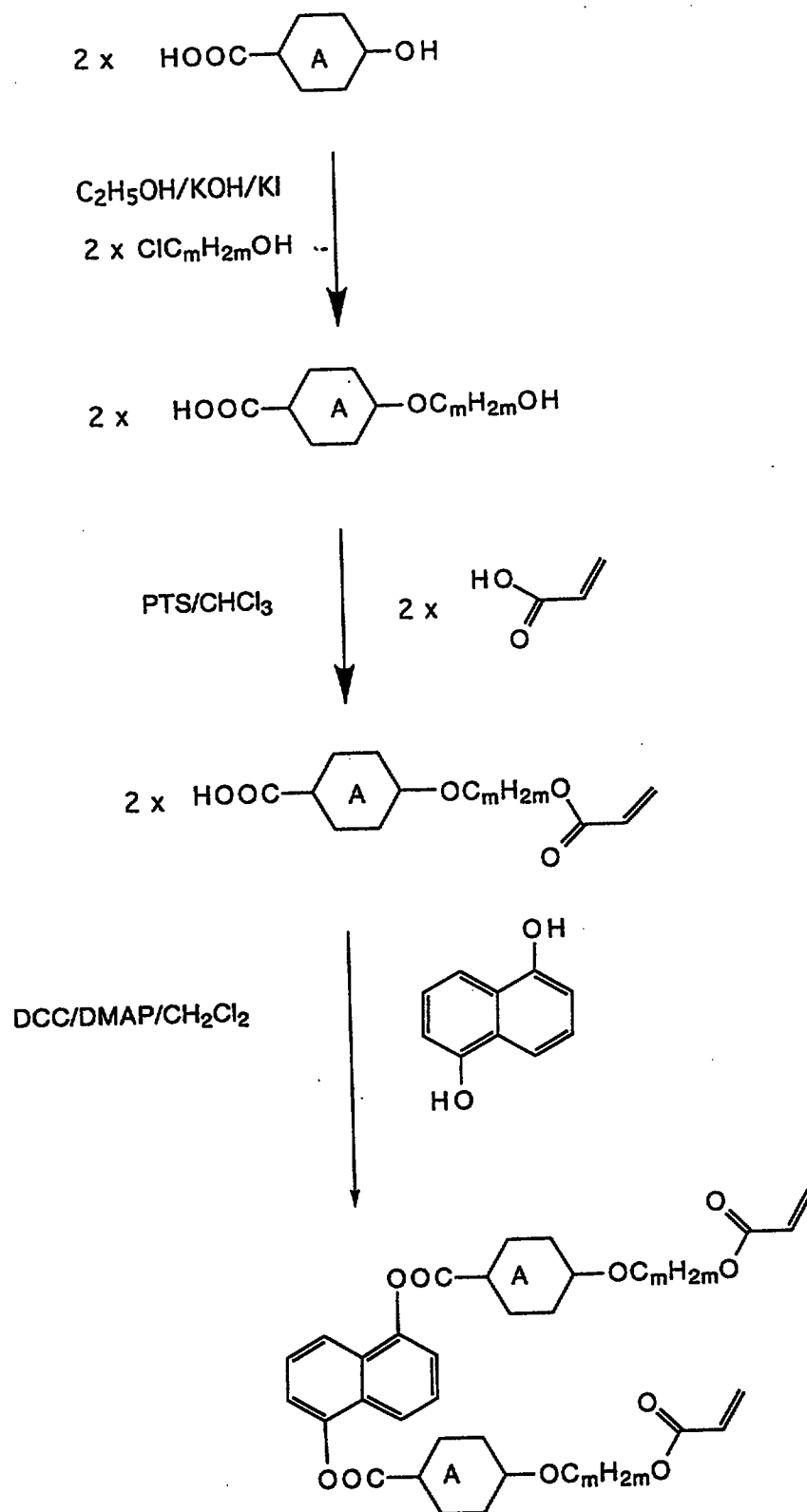
5 The compounds of formula I are very readily accessible
synthetically. Thus, for example, compounds in which Z signifies
a group -OOC- can be produced from 4-[ω -acryloxyalkyloxy]-
benzoic acids and the corresponding naphthohydroquinone (see
Schemes 1 and 2). The esterification can be effected in a manner
10 known per se. A preferred method comprises reacting the
naphthohydroquinone with the carboxylic acid in a polar, but inert
organic solvent (e.g. in dimethylformamide (DMF) or a halogenated
hydrocarbon such as dichloromethane) in the presence of 4-
(dimethylamino)pyridine (DMAP) and N,N'-dicyclohexylcarbo-
15 diimide (DCC). The 4-[ω -acryloxyalkyloxy]benzoic acids are
known per se and can be prepared by alkylating 4-hydroxybenzoic
acid in the presence of a strong base and an ω -halogenated alcohol
as well as potassium iodide and subsequently esterifying the 4-
[ω -hydroxyalkyloxy]benzoic acids with acrylic acid in the
20 presence of p-toluenesulphonic acid (PTA).

The symbols used in the Schemes have the aforementioned
significances.

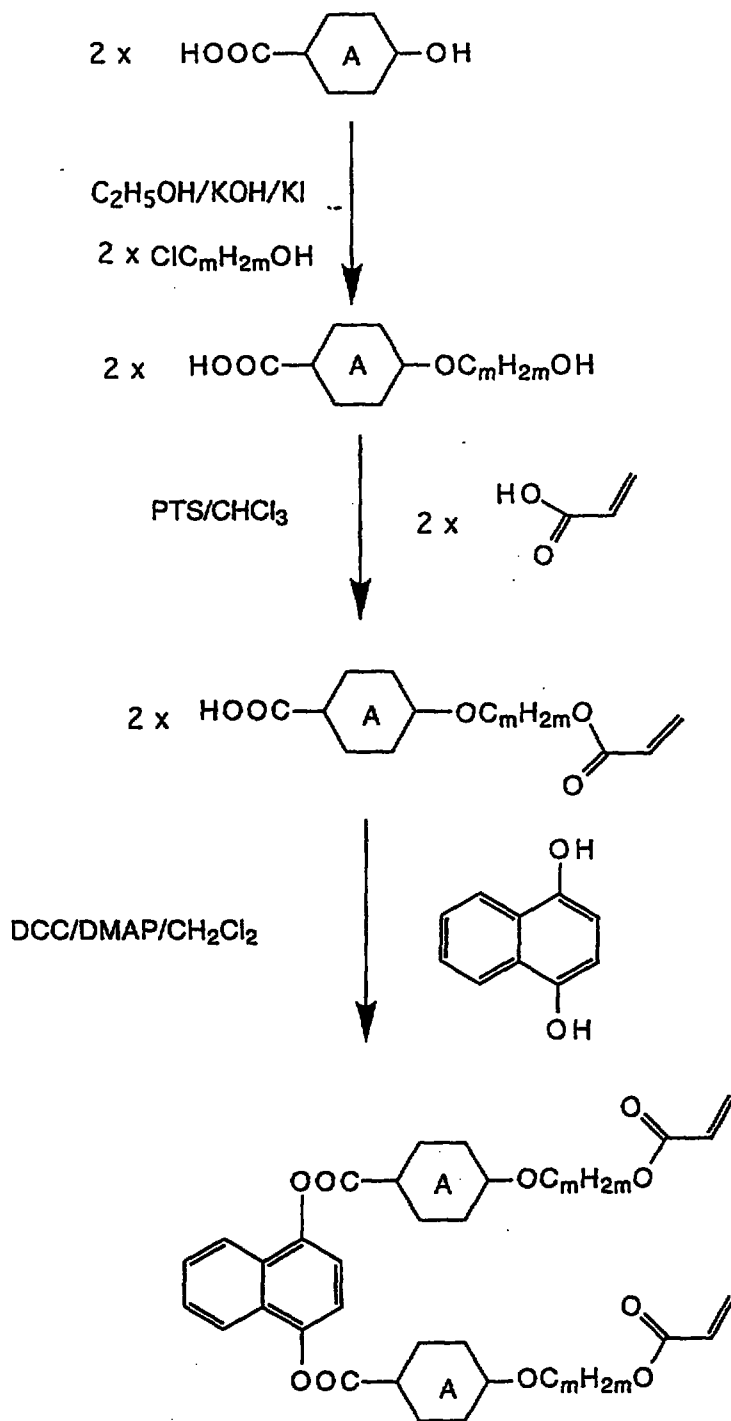
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Scheme 1



Scheme 2



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

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1,4-Bis(4-[ω -acryloyloxyalkyloxy]phenylmethylenoxy)-
naphthalene derivatives, i.e. compounds of formula I in which Z
signifies the group -OCH₂-, can be produced in a manner known
per se by etherifying the corresponding 1,4-naphthohydroquinone
5 with 4-[ω -acryloyloxyalkyloxy)]benzyl alcohols. The reaction can
be effected, for example, in the presence of a dialkyl
azodicarboxylate and triphenylphosphine. The 4-[ω -
acryloyloxyalkyloxy)]benzyl alcohols used as the educt can be
prepared by reducing the reaction product of acrylic acid with
10 4-[ω -hydroxyalkyloxy)]benzyl aldehydes. The 4-[ω -
hydroxyalkyloxy)]benzaldehydes can be prepared by etherifying 4-
hydroxybenzaldehyde with ω -hydroxyalkyl halides in the presence
of usual bases.

15 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.

20 The liquid crystalline mixtures in accordance with the
invention contain at least 2 components, of which at least one
component is a compound of formula I. A second component and
any other components can be additional compounds of formula I or
other known liquid crystalline compounds with or without photo-
cross-linkable groups. One or more chiral components can also be
25 present in the mixture.

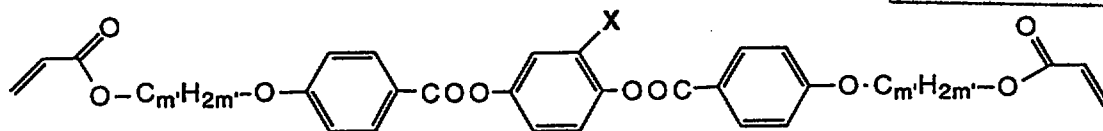
Having regard to the good solubility of the compounds of
formula I and having regard to their good miscibility with one
another, the content of different compounds of formula I in the
30 mixtures in accordance with the invention can be high and can
amount to 100 wt.%.
35

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

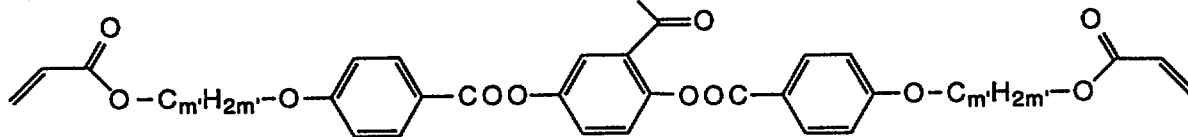
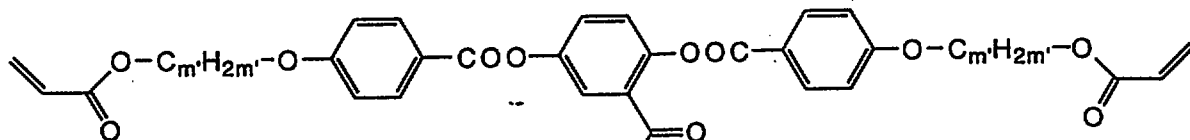
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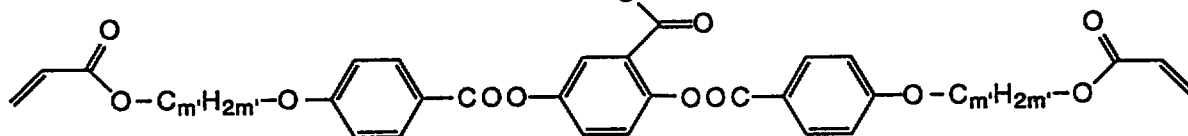
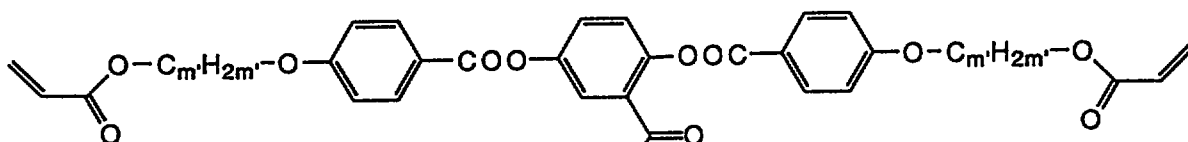
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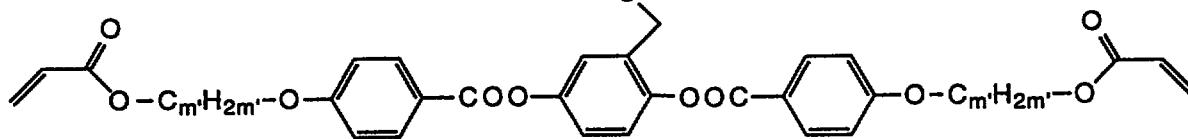
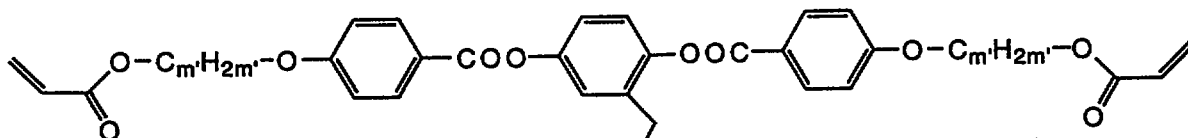
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III



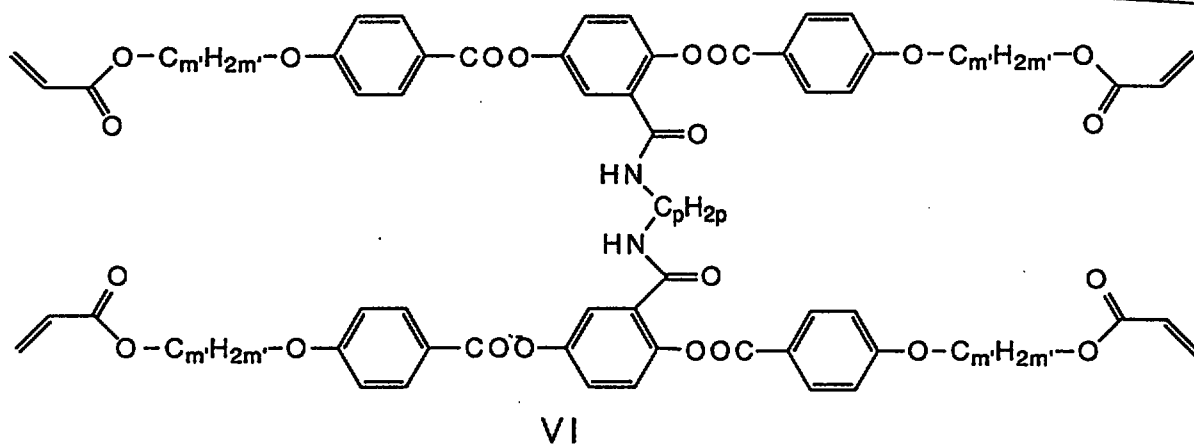
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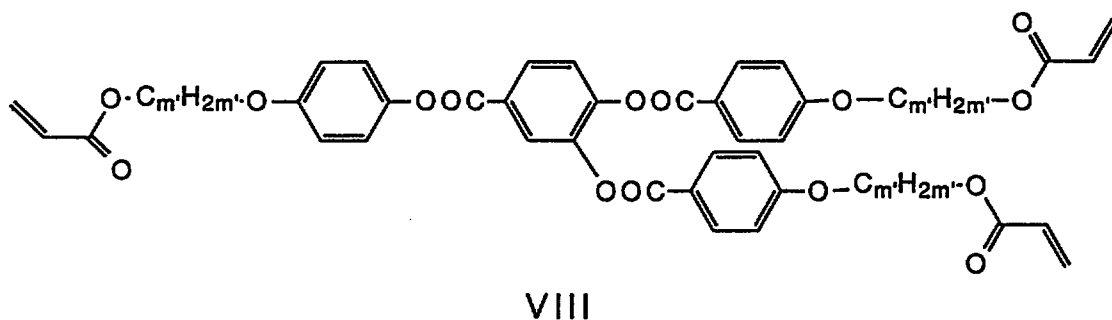
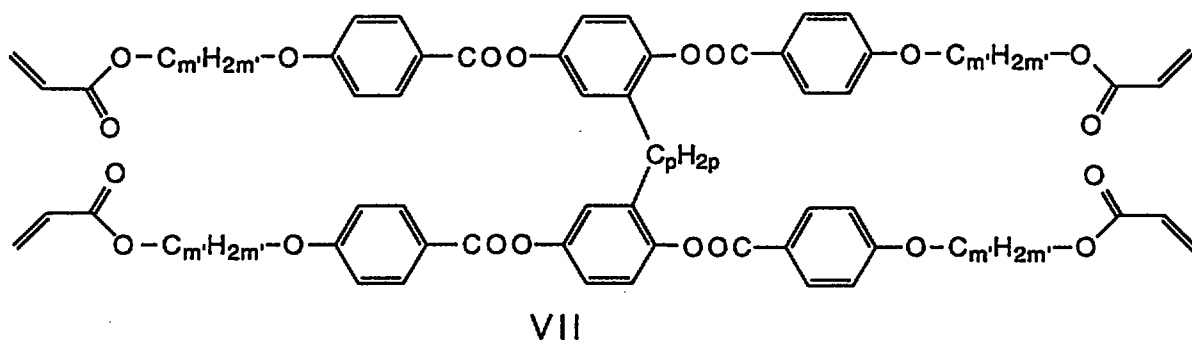
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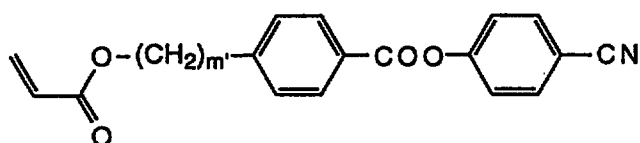
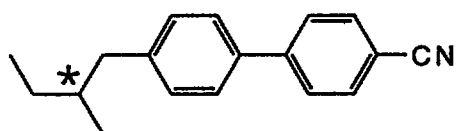
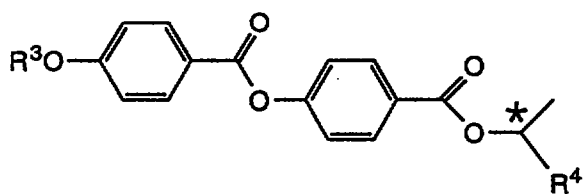




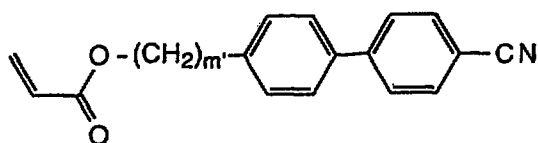
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and



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XII,

wherein

- 5 p signifies a whole number of 2 to 12;
 R^3 and R^4 each independently signify alkyl or alkenyl
 with 2 to 12 carbon atoms;
 X signifies hydrogen, lower alkyl, fluorine,
 bromine, chlorine or cyano;
 10 m' signifies a whole number of 4 to 12; and
 * signifies a centre of chirality.

15 "Lower alkyl" in connection with the compounds of formula
 II embraces methyl, ethyl, propyl, i-propyl, butyl, i-butyl and
 tert.-butyl.

20 The production of the compounds of formula I and of liquid
 crystalline mixtures containing these compounds is illustrated in
 more detail by the following Examples. C signifies a crystalline
 phase, S signifies a smectic phase, N signifies a nematic phase
 and I signifies the isotropic phase.

Example 1

25 0.8 g of N,N'-dicyclohexylcarbodiimide (DCC) was added at
 room temperature while stirring to a solution of 1.25 g of 4-[8-
 acryloyloxyoctyloxy]benzoic acid, 0.25 g of 1,4-naphthohydro-
 quinone and 0.2 g of 4-dimethylaminopyridine (DMAP) in 20 ml of
 dichloromethane. The reaction mixture was stirred at room
 30 temperature overnight, poured into 100 ml of water and then
 extracted three times with 50 ml of dichloromethane 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 subsequently 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 0.2 g of 1,4-bis(4-[8-acryloyloxyoctyloxy]-phenylcarbonyloxy)naphthalene; m.p. (C-N) 94°C, cl.p. (N-I) 104°C.

The following compounds can be prepared in an analogous manner:

- 10 1,4-Bis(4-[3-acryloyloxypropyloxy]phenylcarbonyloxy)-naphthalene;
1,4-bis(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[5-acryloyloxypentyloxy]phenylcarbonyloxy)-naphthalene;
- 15 1,4-bis(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-naphthalene;
1,4-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-naphthalene;
- 20 1,4-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-naphthalene; m.p. (C-I) 106°C, cl.p. (N-I) 98°C;
1,4-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-naphthalene;
- 25 1,5-bis(4-[3-acryloyloxypropyloxy]phenylcarbonyloxy)-naphthalene;
1,5-bis(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[5-acryloyloxypentyloxy]phenylcarbonyloxy)-naphthalene;
- 30 1,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-naphthalene;
1,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)naphthalene;
m.p. (C-I) 130°C, cl.p. (N-I) 108°C;
- 35 1,5-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-naphthalene;



1,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-
naphthalene;

1,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-
naphthalene.

5

Example 2

0.8 g of N,N'-dicyclohexylcarbodiimide is added at room
temperature while stirring to a solution of 1.25 g of 4-[8-vinyl-
10 oxyoctyloxy]]benzoic acid, 0.25 g of 1,4-naphthohydroquinone
and 0.2 g of 4-dimethylaminopyridine in 20 ml of dichloro-
methane. 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 organic
15 phases are combined, 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 cyclohexane/ethyl acetate (vol. 8:2) and
two-fold recrystallization from ethyl alcohol of the fractions
20 which are pure according to thin-layer chromatography gives
0.5 g of 1,4-bis(4-[8-vinyloxyoctyloxy]phenylcarbonyloxy)-
naphthalene.

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

1,4-Bis(4-[3-vinyloxypropyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[4-vinyloxybutyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[5-vinyloxypropyloxy]phenylcarbonyloxy)naphthalene;
30 1,4-bis(4-[6-vinyloxyhexyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[7-vinyloxyheptyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[9-vinyloxynonyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[10-vinyloxydecyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[11-vinyloxyundecyloxy]phenylcarbonyloxy)naphthalene;
35 1,4-bis(4-[12-vinyloxydodecyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[3-vinyloxypropyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[4-vinyloxybutyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[5-vinyloxypropyloxy]phenylcarbonyloxy)naphthalene;



- 1,5-bis(4-[6-vinyloxyhexyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[7-vinyloxyheptyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[8-vinyloxyoctyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[9-vinyloxynonyloxy]phenylcarbonyloxy)naphthalene;
5 1,5-bis(4-[10-vinyloxydecyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[11-vinyloxyundecyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[12-vinyloxydodecyloxy]phenylcarbonyloxy)naphthalene.

Example 3

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- 0.8 g of N,N'-dicyclohexylcarbodiimide is added at room temperature while stirring to a solution of 1.25 g of 4-[7,8-oxiranoctyloxy]benzoic acid, 0.25 g of 1,4-naphthohydroquinone and 0.2 g of 4-dimethylaminopyridine in 20 ml of dichloro-
15 methane. 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
20 subsequently 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 are pure according to thin-layer chromatography gives
25 0.5 g of 1,4-bis(4-[7,8-oxiranoctyloxy]phenylcarbonyloxy)-naphthalene.

The following compounds can be prepared in an analogous manner:

- 30 1,4-Bis(4-[2,3-oxiranpropyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[3,4-oxiranbutyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[4,5-oxiranpentyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[5,6-oxiranhexyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[6,7-oxiranheptyloxy]phenylcarbonyloxy)naphthalene;
35 1,4-bis(4-[8,9-oxirannonyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[9,10-oxirandecyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[10,11-oxiranundecyloxy]phenylcarbonyloxy)-
naphthalene;



- 1,4-bis(4-[11,12-oxirandodecyloxy]phenylcarbonyloxy)-
naphthalene;
1,5-bis(4-[2,3-oxiranpropyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[3,4-oxiranbutyloxy]phenylcarbonyloxy)naphthalene;
5 1,5-bis(4-[4,5-oxiranpentyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[5,6-oxiranhexyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[6,7-oxiranheptyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[7,8-oxiranoctyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[8,9-oxirannonyloxy]phenylcarbonyloxy)naphthalene;
10 1,5-bis(4-[9,10-oxirandecyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[10,11-oxiranundecyloxy]phenylcarbonyloxy)-
naphthalene;
1,5-bis(4-[11,12-oxirandodecyloxy]phenylcarbonyloxy)-
naphthalene.

15

Example 4

- A mixture (C-N, <20°C, N-I, 105°C) of 80 wt.% 1,4-bis(4-[8-
acryloyloxyoctyloxy]phenylcarbonyloxy)naphthalene and 20 wt.%
20 1-chloro-2,5-bis(4-[6-acryloyloxyhexyloxy])phenylcarbonyloxy)-
benzene was provided, treated with 1 wt.% of a photoinitiator
(IRGACURE, Ciba Geigy), dissolved in anisole (40 wt.%) and then
spun on to a glass plate at 2000 revolutions per minute. The glass
plate had previously been coated with poly [methacryloyloxyethyl
25 3-(E)-[4-cyano-4'-biphenyl]acrylate] and then irradiated with
linear polarized light as described in the Swiss Patent
Application CH 2016/94. Thereby, a predetermined structure was
inscribed photolithographically by means of a mask in the (PPN)
layer. The new layer (on the PPN layer) was dried at 90°C on a
30 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 can be used as a
structured optical retarder.

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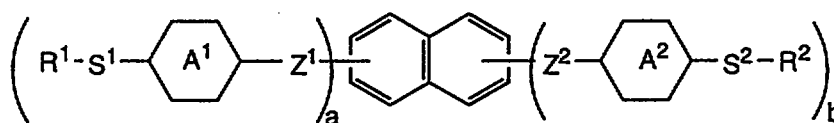




Claims

1. Compounds of the general formula

5



wherein

10

R¹ and R²

each independently signify a cross-linkable group such as ethylene, acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyloxy, vinyl ester, styrene derivative, siloxane, ethyleneimine derivative, maleic acid derivative, fumaric acid derivative or a cinnamic acid derivative, which is optionally substituted with methyl, methoxy, cyano and/or halogen;

15

20

S¹ and S²

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

25

Y

signifies hydrogen, fluorine or methyl;

a

signifies 0 or 1;

b

signifies 1 or 2, with the proviso that a + b = 2;

m

signifies a whole number of 1 to 16;

30

A¹ and A²

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



Z^1 and Z^2 each independently signify a single bond,
-CH₂CH₂-, -OCH₂-, -CH₂O-, -COO-, -OOC-,
-(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-.

5 2. Compounds according to claim 1, wherein the naphthyl
ring is linked in position 1 and 5 or in position 1 and 4 with Z^1
and Z^2 .

10 3. Compounds according to claim 1 or 2, wherein R^1 and
 R^2 have the same significance.

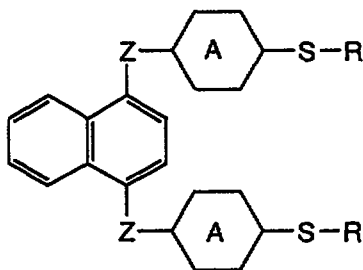
15 4. Compounds according to any one of claims 1 to 3,
wherein R^1 and R^2 signify acrylate, methacrylate, 2-chloro-
acrylate, 2-phenylacrylate, vinyloxy or epoxy.

 5. Compounds according to any one of claims 1 to 4,
wherein S^1 and S^2 have the same significance.

20 6. Compounds according to any one of claims 1 to 5,
wherein Z^1 and Z^2 have the same significance and signify -OCH₂-,
-CH₂O-, -COO- or -OOC-.

25 7. Compounds according to any one of claims 1 to 6,
wherein rings A^1 and A^2 have the same significance and signify
1,4-phenylene or 2- or 3-fluoro-1,4-phenylene.

 8. Compounds according to claim 1 of the general
formulae

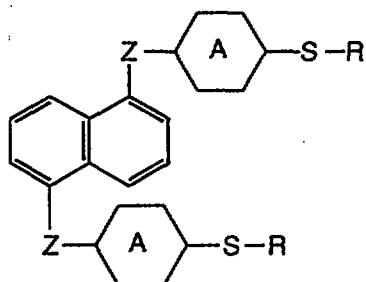


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I-A



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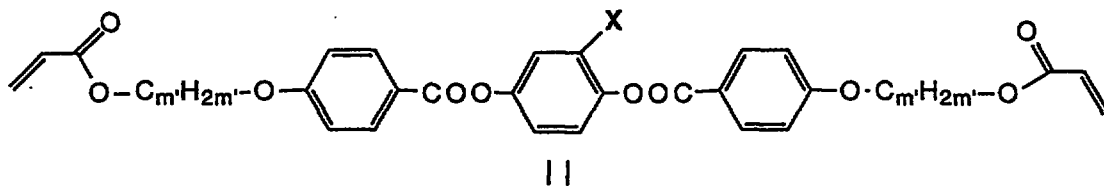
I-B

wherein

- 5 R signifies acrylate, methacrylate,
 2-chloroacrylate, 2-phenylacrylate, vinyloxy
 or epoxy;
- S signifies $-(CH_2)_{m'}-$, $-O(CH_2)_{m'}-$ or $-(CH_2)_{m'}O-$;
- m' is a whole number of 4 to 12;
- 10 A signifies 1,4-phenylene or 2- or 3-fluoro-
 1,4-phenylene; and
- Z signifies $-OCH_2-$ or $-OOC-$.

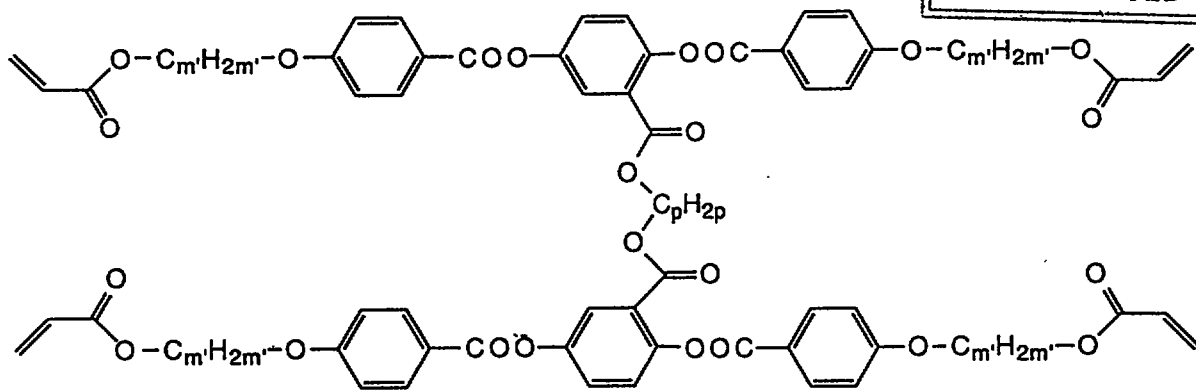
15 9. A cross-linkable mixture consisting of at least 2
 components, of which at least one component is a compound of
 formula I defined in claim 1.

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

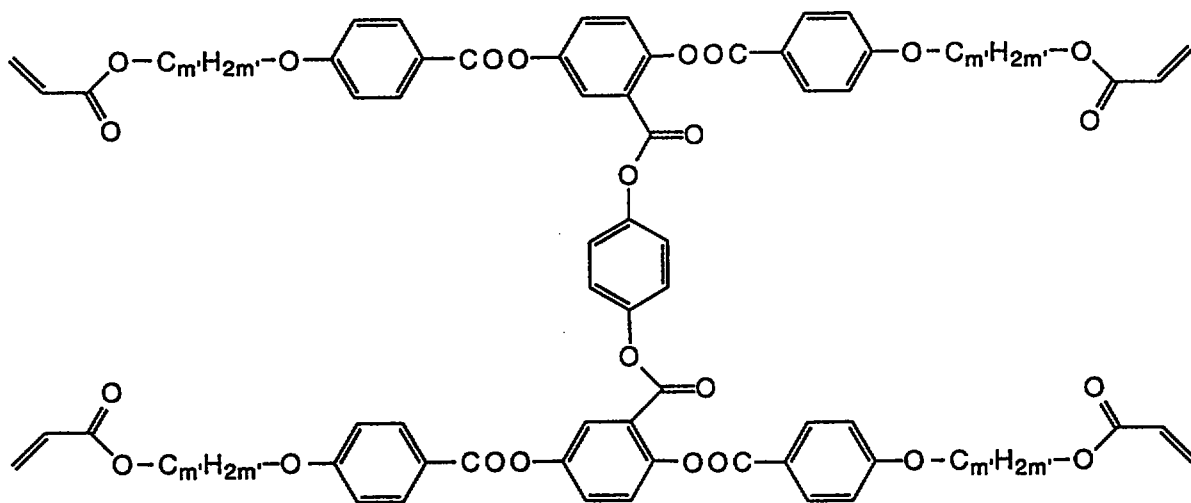




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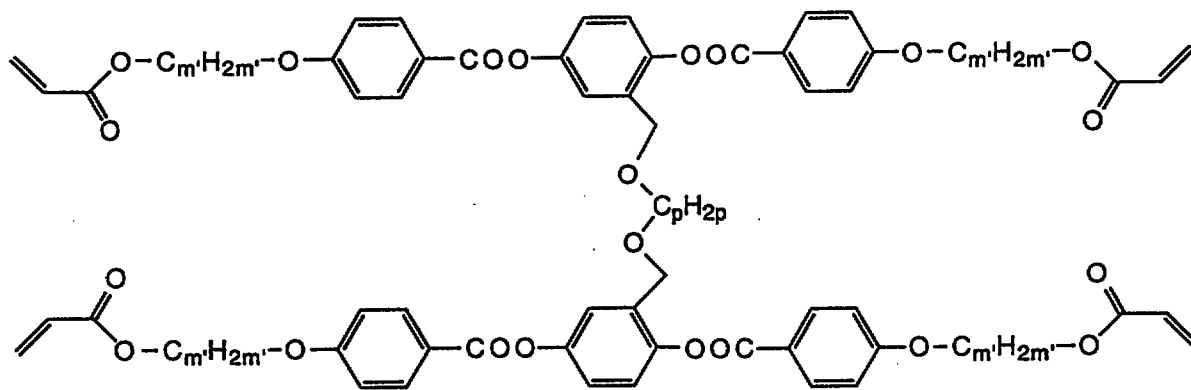


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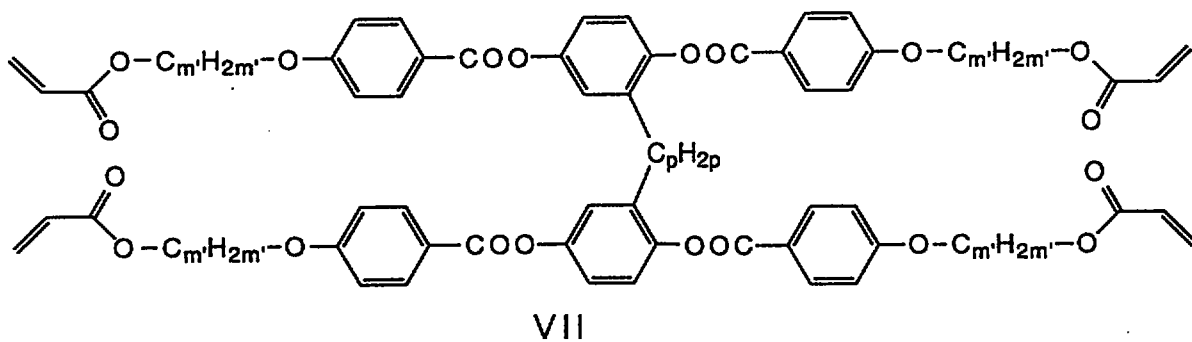
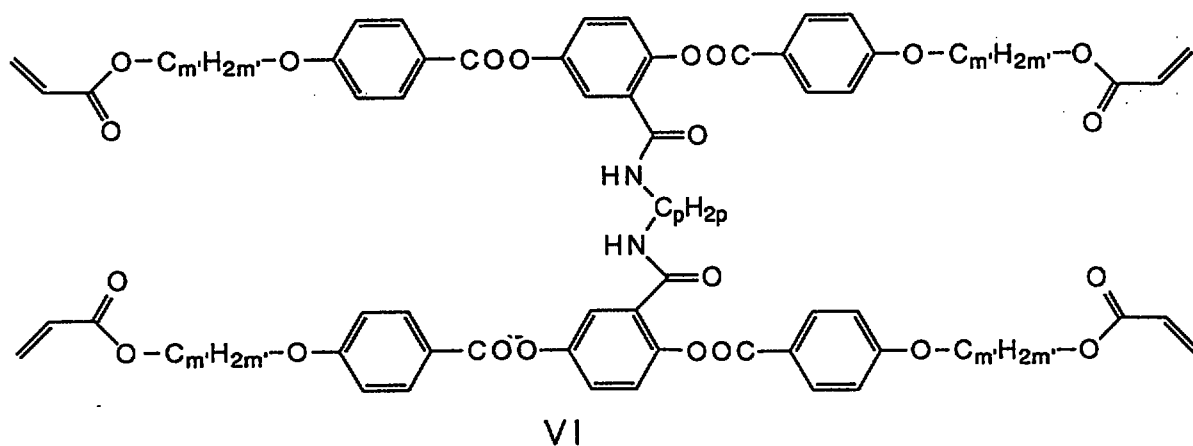


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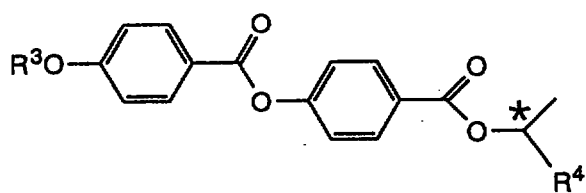
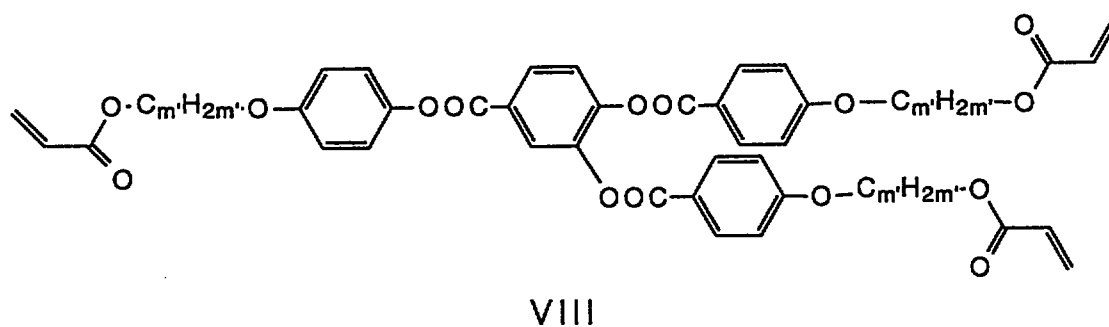
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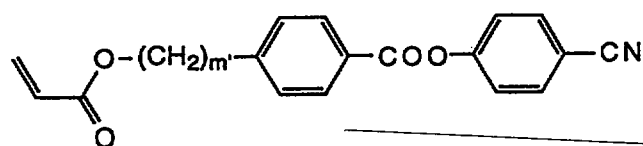
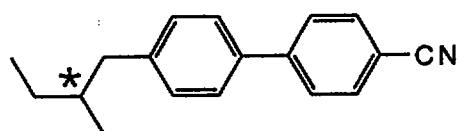
V



5

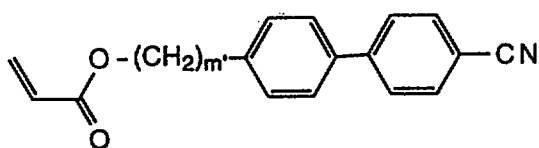


10





and



XII,

wherein

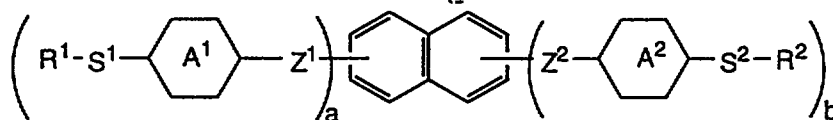
- 5 p signifies a whole number of 2 to 12;
 R³ and R⁴ each independently signify alkyl or alkenyl
 with 2 to 12 carbon atoms;
 X signifies hydrogen, lower alkyl, fluorine,
 bromine, chlorine or cyano;
10 m' signifies a whole number of 4 to 12; and
 * signifies a centre of chirality.

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

15 12. The use of cross-linkable liquid crystalline mixtures
according to claim 9 or 10 in their cross-linked state for optical
components.

Abstract

5 The present invention is concerned with compounds of the general formula



10 wherein
R¹ and R²

each independently signify a cross-linkable group such as ethylene, acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyloxy, vinyl ester, styrene derivative, siloxane, ethyleneimine derivative, maleic acid derivative, fumaric acid derivative or a cinnamic acid derivative, which is optionally substituted with methyl, methoxy, cyano and/or halogen;

15 S¹ and S² signify -(CY₂)_m-, -O(CY₂)_m-, -(CY₂)_mO-, -(CY₂)_mCOO-, -(CY₂)_mOOC-, -(Si[(CH₃)₂O])_m-, -OCH₂(Si[(CH₃)₂O])_mSi[(CH₃)₂]CH₂O- or -NHCH₂(Si[(CH₃)₂O])_mSi[(CH₃)₂]CH₂NH-;

20 Y signifies hydrogen, fluorine or methyl;
30 a signifies 0 or 1;
b signifies 1 or 2, with the proviso that a + b = 2;

m signifies a whole number of 1 to 16;
35 A¹ and A² each independently signify 1,4-phenylene, which is optionally mono- or multiply-substituted with halogen, cyano, methyl, methoxy and/or acetyl, pyridine-2,5-diyl,



pyrimidine-2,5-diyl, trans-1,4-cyclo-
hexylene or trans-1,3-dioxane-2,5-diyl;
and

Z¹ and Z²

5

each independently signify a single bond,
-CH₂CH₂-, -OCH₂-, -CH₂O-, -COO-, -OOC-,
-(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-,

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

10

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PHOTO CROSS-LINKABLE NAPHTHALENE DERIVATIVES

The present invention is concerned with photo cross-linkable naphthyl derivatives, mixtures which contain such compounds and their use in the cross-linked state for optical 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 thereby produced remains even at high temperatures. Such layers can be, for example, parts of hybrid layers, as are described in Swiss Patent Applications CH 2016/94 and CH 2017/94. Thus, optical components such as, for example, retarders, wave guides, optical grids and filters, integrated colour filters or cells having piezoelectric properties and those having non-linear optical (NLO) properties, etc., can be produced. Such optical components are used, 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 use. For example, materials for optical retarders should have a high birefringence in order that the layer thickness of the integrated optical component can be held at a minimum.

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, reduces the thermal expansion coefficient and avoids microdistortion losses. This leads to an increased mechanical stability.

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

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

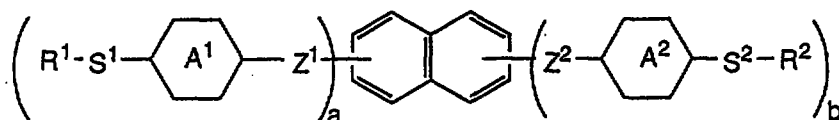
There is accordingly the need, especially for use in optical filters, to produce photochemically oligomerisable or polymerisable compounds which are distinguished by an especially high optical anisotropy and which at the same time have low melting points and clearing points in order that they can be 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

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and also 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 liquid crystal mixtures for optical components, namely compounds of the general formula



wherein

R¹ and R²

each independently signify a cross-linkable group such as ethylene, acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyloxy, vinyl ester, styrene derivative, siloxane, ethyleneimine derivative, maleic acid derivative, fumaric acid derivative or a cinnamic acid derivative, which is optionally substituted with methyl, methoxy, cyano and/or halogen;

S¹ and S²

signify $-(CY_2)_m-$, $-O(CY_2)_m-$, $-(CY_2)_mO-$, $-(CY_2)_mCOO-$, $-(CY_2)_mOOC-$, $-(Si[(CH_3)_2]O)_m-$, $-OCH_2(Si[(CH_3)_2]O)_mSi[(CH_3)_2]CH_2O-$ or $-NHCH_2(Si[(CH_3)_2]O)_mSi[(CH_3)_2]CH_2NH-$;

Y

signifies hydrogen, fluorine or methyl;

a

signifies 0 or 1;

b

signifies 1 or 2, with the proviso that $a + b = 2$;

m

signifies a whole number of 1 to 16;

A¹ and A²

each independently signify 1,4-phenylene, which is optionally mono- or multiply-substituted with halogen, cyano, methyl,

- 4 -

methoxy and/or acetyl, pyridine-2,5-diyl,
pyrimidine-2,5-diyl, trans-1,4-cyclo-
hexylene or trans-1,3-dioxane-2,5-diyl;
and

Z¹ and Z²

each independently signify a single bond,
-CH₂CH₂-, -OCH₂-, -CH₂O-, -COO-, -OOC-,
-(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-.

The compounds of general formula I are distinguished by their relatively low viscosity. They can accordingly be applied without problems to a suitable surface. This generally 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 by the application of an electric field.

The term "1,4-phenylene, which is mono- or multiply-substituted with halogen, cyano, methyl, methoxy and/or acetyl," embraces in the scope of the present invention 1,4-phenylene, 1,4-phenylene substituted with fluorine, bromine, chlorine, cyano, methyl, methoxy or acetyl, such as, for example 2- or 3-fluoro-1,4-phenylene, 2,3-, 2,6- or 3,5-difluoro-1,4-phenylene, 2- or 3-chloro-1,4-phenylene, 2,3-, 2,6- or 3,5-dichloro-1,4-phenylene, 2- or 3-bromo-1,4-phenylene, 2- or 3-cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene, 2- or 3-acetyl-1,4-phenylene, 2- or 3-methyl-1,4-phenylene, 2- or 3-methoxy-1,4-phenylene, and the like. Especially preferred compounds of formula I are those in which rings A¹ and A² are the same and signify 1,4-phenylene or 2- or 3-fluoro-1,4-phenylene.

The spacer groups S¹ and S² can also be chiral, if desired. Preferred compounds of formula I are those in which S¹ and S² have the same significance. Preferred spacer groups are those in which Y signifies hydrogen and m is a whole number of 4 to 12.

Preferred residues R¹ and R² are acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-phenylacrylamide, epoxy, vinyloxy, vinyl

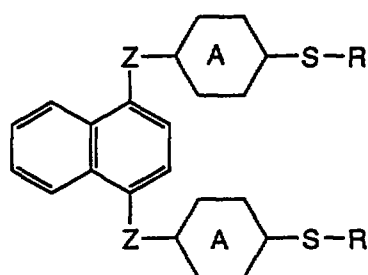
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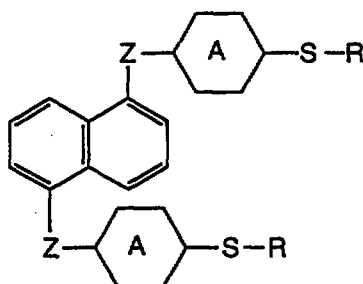
ester, styrene derivatives, maleic acid derivatives, fumaric acid derivatives and the like. It is these residues which can be cross-linked photochemically after coating the suitable carrier with compounds of formula I. In particular, there are preferred those compounds of formula I in which the residues R^1 and R^2 have the same significance. They preferably signify acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, vinyloxy or epoxy.

Especially preferred compounds of formula I are those in which the naphthyl ring is linked in position 1 and 5 or in position 1 and 4 with Z^1 and Z^2 , especially those in which Z^1 and Z^2 are the same and signify $-OCH_2-$, $-CH_2O-$, $-COO-$ or $-OOC-$.

Compounds which are quite especially preferred are those of the formulae



I-A



I-B

wherein

- | | |
|------|--|
| R | signifies acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, vinyloxy or epoxy; |
| S | signifies $-(CH_2)_{m'}-$, $-O(CH_2)_{m'}-$ or $-(CH_2)_{m'}O-$; |
| m' | is a whole number of 4 to 12; |

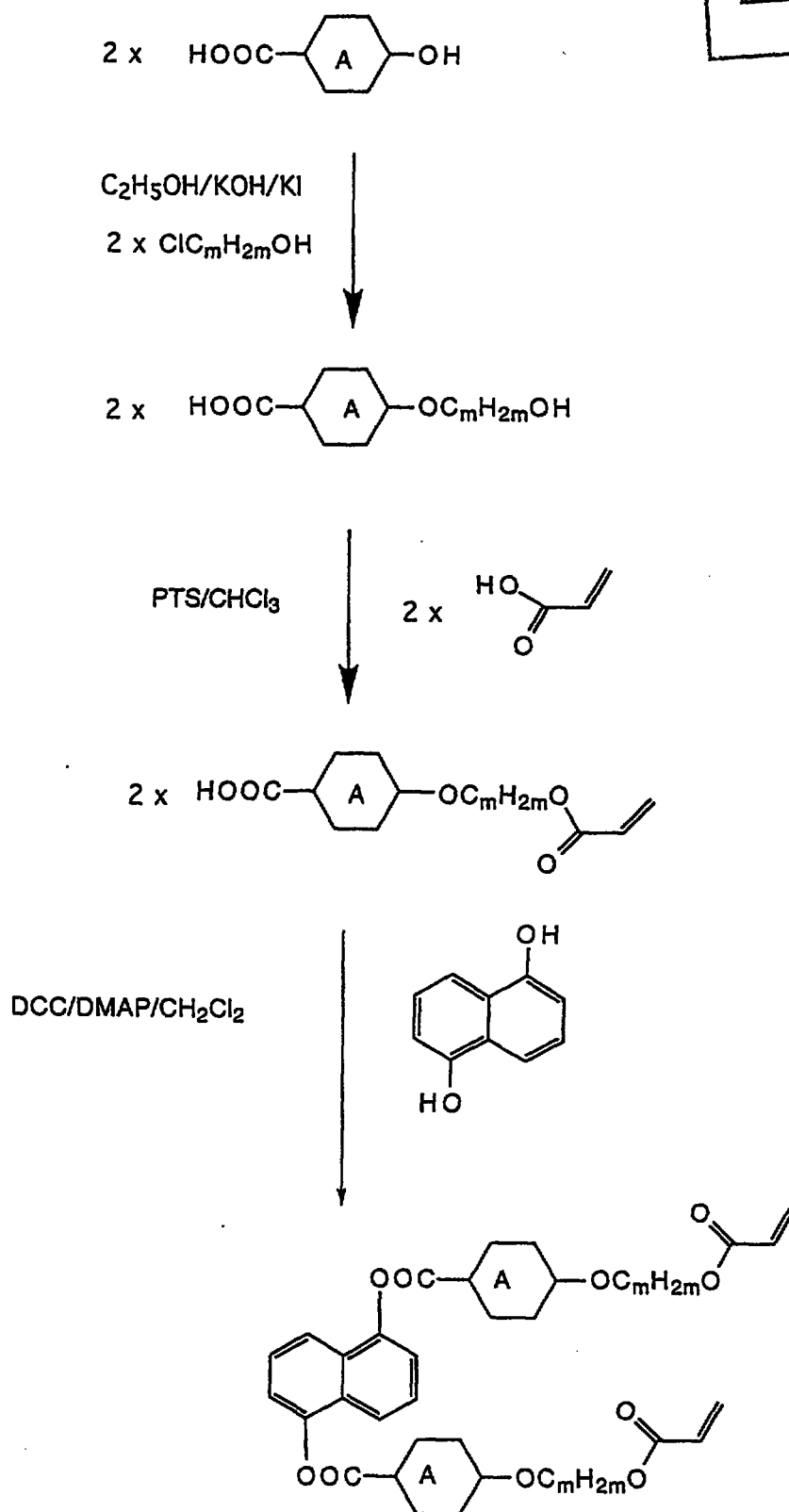
- A signifies 1,4-phenylene or 2- or 3-fluoro-1,4-phenylene; and
- Z signifies -OCH₂- or -OOC-.

The compounds of formula I are very readily accessible synthetically. Thus, for example, compounds in which Z signifies a group -OOC- can be produced from 4-[ω -acryloxyalkyloxy]-benzoic acids and the corresponding naphthohydroquinone (see Schemes 1 and 2). The esterification can be effected in a manner known per se. A preferred method comprises reacting the naphthohydroquinone with the carboxylic acid in a polar, but inert organic solvent (e.g. in dimethylformamide (DMF) or a halogenated hydrocarbon such as dichloromethane) in the presence of 4-(dimethylamino)pyridine (DMAP) and N,N'-dicyclohexylcarbodiimide (DCC). The 4-[ω -acryloxyalkyloxy]benzoic acids are known per se and can be prepared by alkylating 4-hydroxybenzoic acid in the presence of a strong base and an ω -halogenated alcohol as well as potassium iodide and subsequently esterifying the 4-[ω -hydroxyalkyloxy]benzoic acids with acrylic acid in the presence of p-toluenesulphonic acid (PTA).

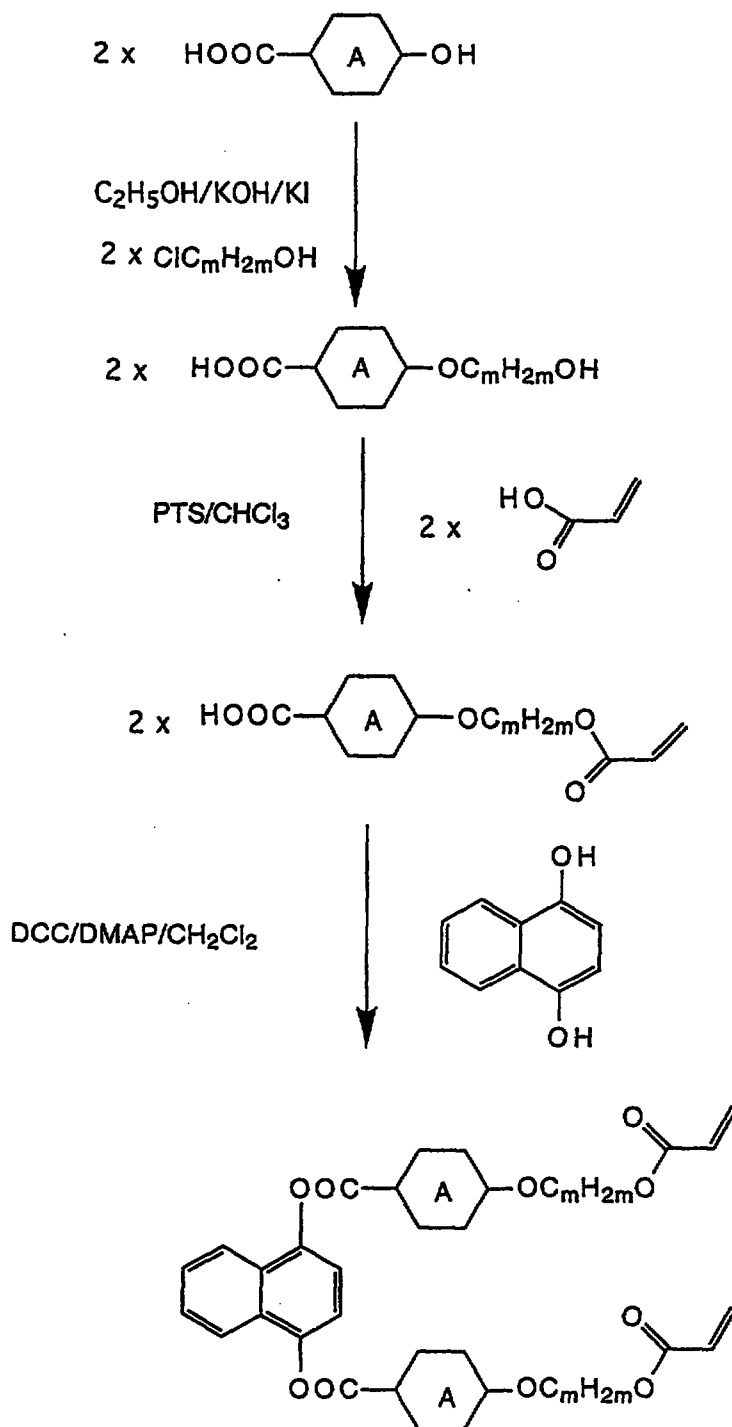
The symbols used in the Schemes have the aforementioned significances.

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Scheme 1



Scheme 2



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

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1,4-Bis(4-[ω -acryloyloxyalkyloxy]phenylmethylenoxy)naphthalene derivatives, i.e. compounds of formula I in which Z signifies the group -OCH₂-, can be produced in a manner known per se by etherifying the corresponding 1,4-naphthohydroquinone with 4-[ω -acryloyloxyalkyloxy]]benzyl alcohols. The reaction can be effected, for example, in the presence of a dialkyl azodicarboxylate and triphenylphosphine. The 4-[ω -acryloyloxyalkyloxy]]benzyl alcohols used as the educt can be prepared by reducing the reaction product of acrylic acid with 4-[ω -hydroxyalkyloxy]]benzyl aldehydes. The 4-[ω -hydroxyalkyloxy]]benzaldehydes can be prepared by etherifying 4-hydroxybenzaldehyde with ω -hydroxyalkyl halides in the presence of usual bases.

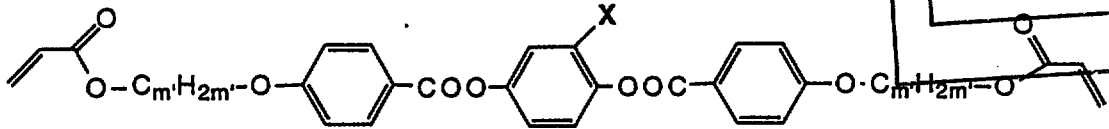
The compounds of formula I can be used as single compounds or in the form of mixtures with one another and/or with other liquid crystal components.

The liquid crystalline mixtures in accordance with the invention contain at least 2 components, of which at least one component is a compound of formula I. A second component and any other components can be additional compounds of formula I or other known liquid crystalline compounds with or without photocross-linkable groups. One or more chiral components can also be present in the mixture.

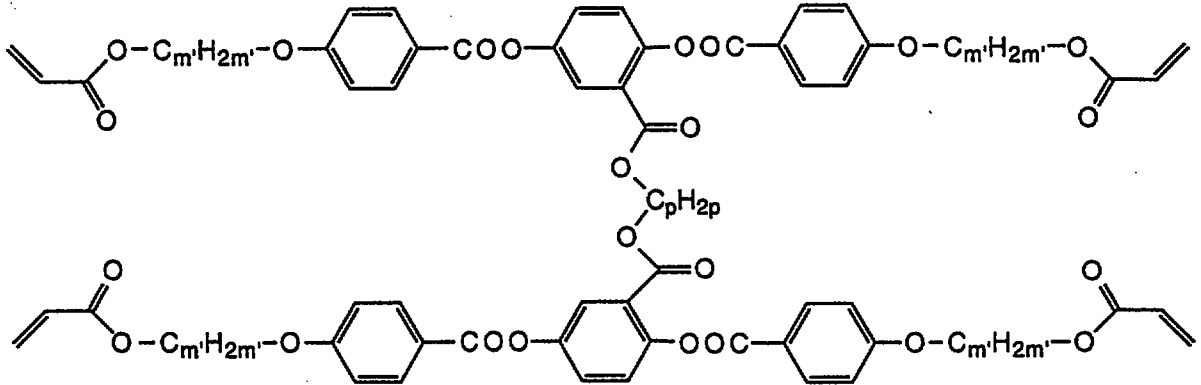
Having regard to the good solubility of the compounds of formula I and having regard to their good miscibility with one another, the content of different compounds of formula I in the mixtures in accordance with the invention can be high and can amount to 100 wt.%.

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

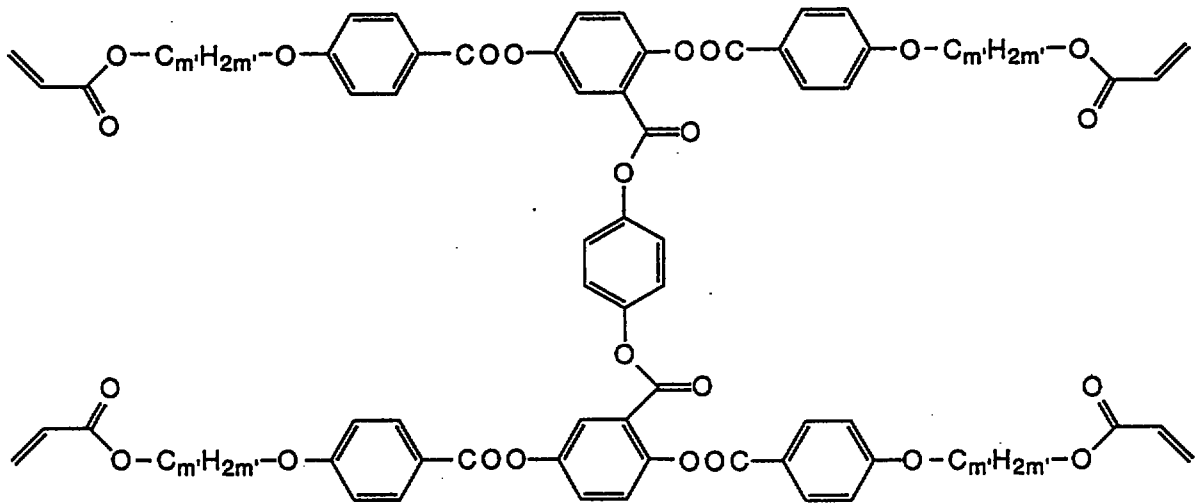
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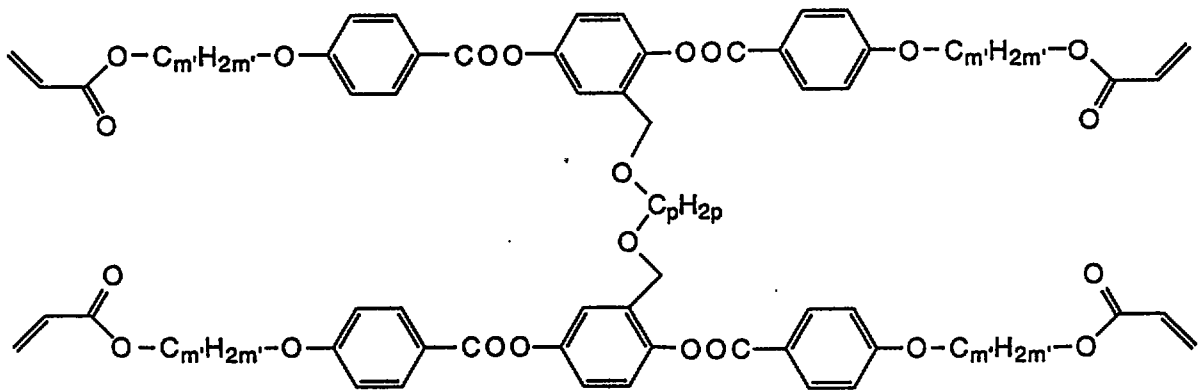
II



III



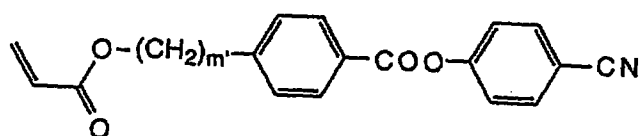
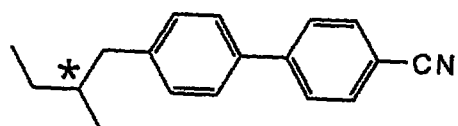
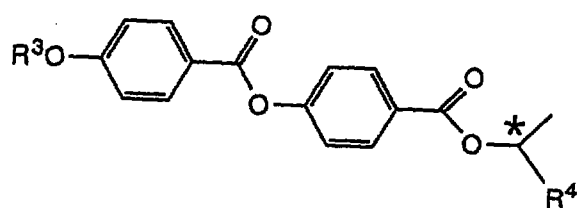
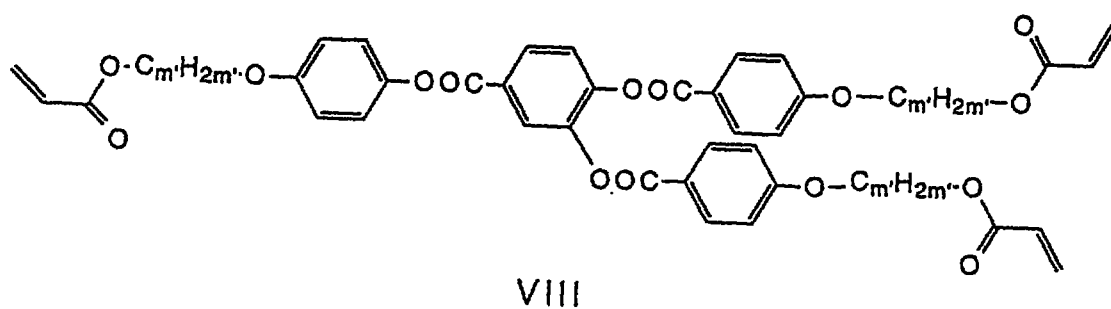
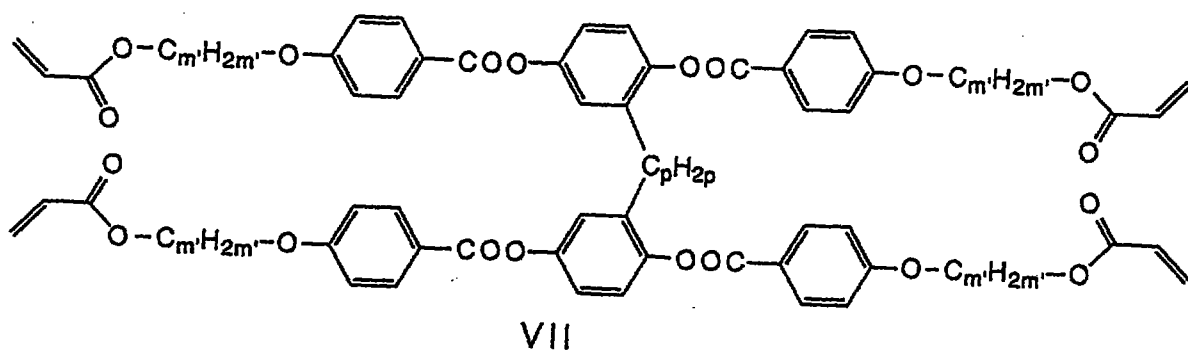
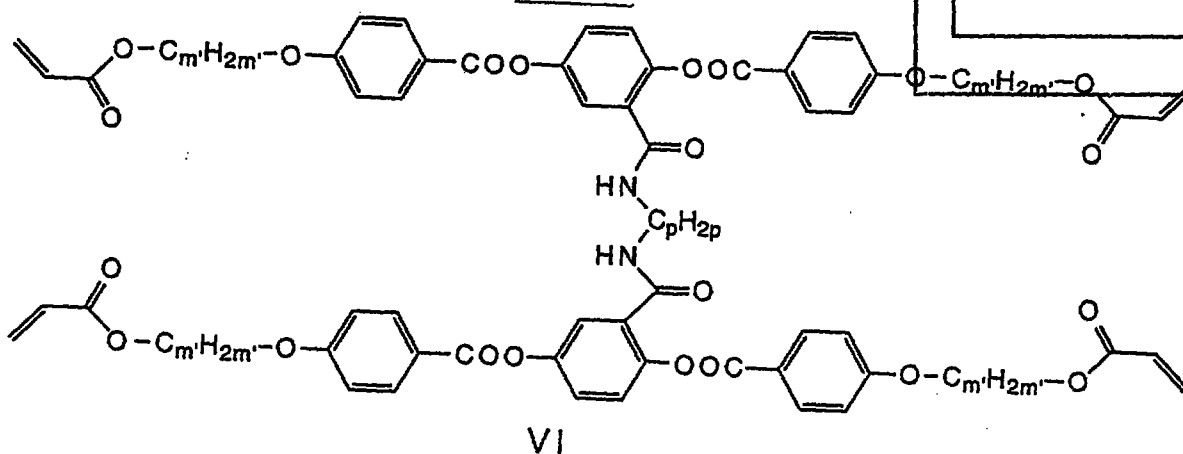
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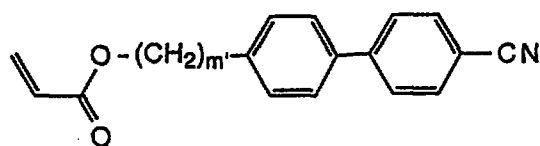
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and



XII,

wherein

- p signifies a whole number of 2 to 12;
- R^3 and R^4 each independently signify alkyl or alkenyl with 2 to 12 carbon atoms;
- X signifies hydrogen, lower alkyl, fluorine, bromine, chlorine or cyano;
- m' signifies a whole number of 4 to 12; and
- * signifies a centre of chirality.

"Lower alkyl" in connection with the compounds of formula II embraces methyl, ethyl, propyl, i-propyl, butyl, i-butyl and tert.-butyl.

The production of the compounds of formula I and of liquid crystalline mixtures containing these compounds is illustrated in more detail by the following Examples. C signifies a crystalline phase, S signifies a smectic phase, N signifies a nematic phase and I signifies the isotropic phase.

Example 1

0.8 g of N,N'-dicyclohexylcarbodiimide (DCC) was added at room temperature while stirring to a solution of 1.25 g of 4-[8-acryloyloxyoctyloxy]benzoic acid, 0.25 g of 1,4-naphthohydroquinone and 0.2 g of 4-dimethylaminopyridine (DMAP) in 20 ml of dichloromethane. The reaction mixture was stirred at room temperature overnight, poured into 100 ml of water and then extracted three times with 50 ml of dichloromethane each time. The organic phases were combined, washed twice with 100 ml of water each time, dried over magnesium sulphate, filtered and the filtrate was subsequently concentrated. Chromatographic

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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 0.2 g of 1,4-bis(4-[8-acryloyloxyoctyloxy]-phenylcarbonyloxy)naphthalene; m.p. (C-N) 94°C, cl.p. (N-I) 104°C.

The following compounds can be prepared in an analogous manner:

1,4-Bis(4-[3-acryloyloxypropyloxy]phenylcarbonyloxy)-naphthalene;
1,4-bis(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[5-acryloyloxypentyloxy]phenylcarbonyloxy)-naphthalene;
1,4-bis(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-naphthalene;
1,4-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-naphthalene;
1,4-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-naphthalene; m.p. (C-I) 106°C, cl.p. (N-I) 98°C;
1,4-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-naphthalene;
1,5-bis(4-[3-acryloyloxypropyloxy]phenylcarbonyloxy)-naphthalene;
1,5-bis(4-[4-acryloyloxybutyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[5-acryloyloxypentyloxy]phenylcarbonyloxy)-naphthalene;
1,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[7-acryloyloxyheptyloxy]phenylcarbonyloxy)-naphthalene;
1,5-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)naphthalene; m.p. (C-I) 130°C, cl.p. (N-I) 108°C;
1,5-bis(4-[9-acryloyloxynonyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[10-acryloyloxydecyloxy]phenylcarbonyloxy)-naphthalene;

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1,5-bis(4-[11-acryloyloxyundecyloxy]phenylcarbonyloxy)-
naphthalene;
1,5-bis(4-[12-acryloyloxydodecyloxy]phenylcarbonyloxy)-
naphthalene.

Example 2

0.8 g of N,N'-dicyclohexylcarbodiimide is added at room temperature while stirring to a solution of 1.25 g of 4-[8-vinyloxyoctyloxy]benzoic acid, 0.25 g of 1,4-naphthohydroquinone and 0.2 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 organic phases are combined, 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 cyclohexane/ethyl acetate (vol. 8:2) and two-fold recrystallization from ethyl alcohol of the fractions which are pure according to thin-layer chromatography gives 0.5 g of 1,4-bis(4-[8-vinyloxyoctyloxy]phenylcarbonyloxy)-naphthalene.

The following compounds can be prepared in an analogous manner:

1,4-Bis(4-[3-vinyloxypropyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[4-vinyloxybutyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[5-vinyloxypropyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[6-vinyloxyhexyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[7-vinyloxyheptyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[9-vinyloxynonyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[10-vinyloxydecyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[11-vinyloxyundecyloxy]phenylcarbonyloxy)naphthalene;
1,4-bis(4-[12-vinyloxydodecyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[3-vinyloxypropyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[4-vinyloxybutyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[5-vinyloxypropyloxy]phenylcarbonyloxy)naphthalene;

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- 1,5-bis(4-[6-vinyloxyhexyloxy]phenylcarbonyloxy)naphthalene;
- 1,5-bis(4-[7-vinyloxyheptyloxy]phenylcarbonyloxy)naphthalene;
- 1,5-bis(4-[8-vinyloxyoctyloxy]phenylcarbonyloxy)naphthalene;
- 1,5-bis(4-[9-vinyloxynonyloxy]phenylcarbonyloxy)naphthalene;
- 1,5-bis(4-[10-vinyloxydecyloxy]phenylcarbonyloxy)naphthalene;
- 1,5-bis(4-[11-vinyloxyundecyloxy]phenylcarbonyloxy)naphthalene;
- 1,5-bis(4-[12-vinyloxydodecyloxy]phenylcarbonyloxy)naphthalene.

Example 3

0.8 g of N,N'-dicyclohexylcarbodiimide is added at room temperature while stirring to a solution of 1.25 g of 4-[7,8-oxiranoctyloxy]benzoic acid, 0.25 g of 1,4-naphthohydroquinone and 0.2 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 cyclohexane/ethyl acetate (vol. 8:2) and two-fold recrystallization from ethyl alcohol of the fractions which are pure according to thin-layer chromatography gives 0.5 g of 1,4-bis(4-[7,8-oxiranoctyloxy]phenylcarbonyloxy)-naphthalene.

The following compounds can be prepared in an analogous manner:

- 1,4-Bis(4-[2,3-oxiranpropyloxy]phenylcarbonyloxy)naphthalene;
- 1,4-bis(4-[3,4-oxiranbutyloxy]phenylcarbonyloxy)naphthalene;
- 1,4-bis(4-[4,5-oxiranpentyloxy]phenylcarbonyloxy)naphthalene;
- 1,4-bis(4-[5,6-oxiranhexyloxy]phenylcarbonyloxy)naphthalene;
- 1,4-bis(4-[6,7-oxiranheptyloxy]phenylcarbonyloxy)naphthalene;
- 1,4-bis(4-[8,9-oxirannonyloxy]phenylcarbonyloxy)naphthalene;
- 1,4-bis(4-[9,10-oxirandecyloxy]phenylcarbonyloxy)naphthalene;
- 1,4-bis(4-[10,11-oxiranundecyloxy]phenylcarbonyloxy)-naphthalene;

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1,4-bis(4-[11,12-oxirandodecyloxy]phenylcarbonyloxy)-naphthalene;
1,5-bis(4-[2,3-oxiranpropyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[3,4-oxiranbutyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[4,5-oxiranpentyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[5,6-oxiranhexyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[6,7-oxiranheptyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[7,8-oxiranoctyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[8,9-oxirannonyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[9,10-oxirandecyloxy]phenylcarbonyloxy)naphthalene;
1,5-bis(4-[10,11-oxiranundecyloxy]phenylcarbonyloxy)-naphthalene;
1,5-bis(4-[11,12-oxirandodecyloxy]phenylcarbonyloxy)-naphthalene.

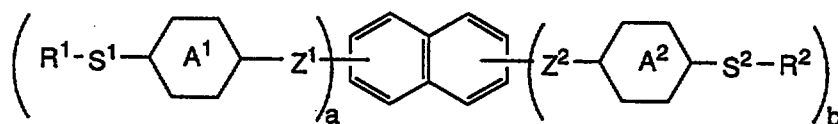
Example 4

A mixture (C-N, <20°C, N-I, 105°C) of 80 wt.% 1,4-bis(4-[8-acryloyloxyoctyloxy]phenylcarbonyloxy)naphthalene and 20 wt.% 1-chloro-2,5-bis(4-[6-acryloyloxyhexyloxy]phenylcarbonyloxy)-benzene was provided, treated with 1 wt.% of a photoinitiator (IRGACURE, Ciba Geigy), dissolved in anisole (40 wt.%) and then spun on to a glass plate at 2000 revolutions per minute. The glass plate had previously been coated with poly [methacryloyloxyethyl 3-(E)-[4-cyano-4'-biphenyl]acrylate] and then irradiated with linear polarized light as described in the Swiss Patent Application CH 2016/94. Thereby, a predetermined structure was inscribed photolithographically by means of a mask in the (PPN) layer. The 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 can be used as a structured optical retarder.

PHOTO CROSS-LINKABLE NAPHTHALENE DERIVATIVES

Abstract

The present invention is concerned with compounds of the general formula



wherein

R¹ and R²

each independently signify a cross-linkable group such as ethylene, acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, epoxy, itaconic acid ester, vinyloxy, vinyl ester, styrene derivative, siloxane, ethyleneimine derivative, maleic acid derivative, fumaric acid derivative or a cinnamic acid derivative, which is optionally substituted with methyl, methoxy, cyano and/or halogen;

S¹ and S²

signify $-(CY_2)_m-$, $-O(CY_2)_m-$, $-(CY_2)_mO-$, $-(CY_2)_mCOO-$, $-(CY_2)_mOOC-$, $-(Si[(CH_3)_2O])_m-$, $-OCH_2(Si[(CH_3)_2O])_mSi[(CH_3)_2]CH_2O-$ or $-NHCH_2(Si[(CH_3)_2O])_mSi[(CH_3)_2]CH_2NH-$;

Y

signifies hydrogen, fluorine or methyl;

a

signifies 0 or 1;

b

signifies 1 or 2, with the proviso that $a + b = 2$;

m

signifies a whole number of 1 to 16;

A¹ and A²

each independently signify 1,4-phenylene, which is optionally mono- or multiply-substituted with halogen, cyano, methyl, methoxy and/or acetyl, pyridine-2,5-diyl,

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pyrimidine-2,5-diyl, trans-1,4-cyclo-
hexylene or trans-1,3-dioxane-2,5-diyl;
and

Z¹ and Z²

each independently signify a single bond,
-CH₂CH₂-, -OCH₂-, -CH₂O-, -COO-, -OOC-,
-(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-,

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