

Optically active materials

This invention relates to optically active materials and their use as doping agents for liquid crystals for a wide range of applications including solid state cholesteric filters for projection displays, circular polarisers, optical filters, etc.

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The addition of an optically-active compound to a non-optically-active liquid crystalline phase is one of procedures used for the conversion of non-optically-active into optically-active mesophases. The nematic phase, for example, is converted to the cholesteric one when being doped with a small amount of an optically-active substance.

10 This conversion manifests itself by the occurrence of an intermolecular helix which is characterised by the so-called helical twisting power (HTP) given in Equation 1:

$$HTP = \left| \frac{dp^{-1}}{dx} \right|_{x=0} \equiv \frac{p^{-1}}{x} = \sum_i x_i (HTP)_i \quad (1)$$

- 15 HTP (μm^{-1}) helical twisting power for small concentrations
 p (μm) pitch of induced helix, + for (*P*)-helix, – for (*M*)-helix
 x mole fraction of the dopant
 $\sum_i$ sum over all optically-active conformers of the dopant
 x_i mole fraction of conformer *i*

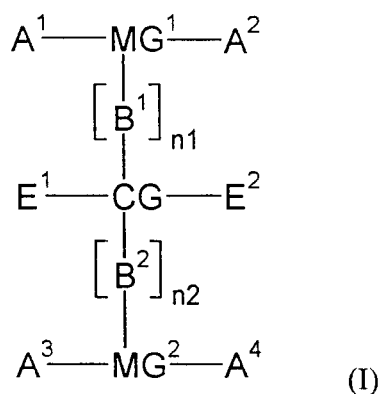
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Said HTP is in fact a measure for the efficiency of a given dopant and is determined by the *Cano* method with solutions of the dopant in the host mesophase. Since the optically-active guest and the non-optically-active host compounds are not necessarily compatible at the molecular scale, their binary solution is frequently characterised by
 25 undesirable changes of the thermotropic sequence of the initial host liquid crystalline material, like for example a depression of the clearing point. Those changes could in turn have negative effects on the phase properties of the host, such as a decrease of the birefringence etc. Therefore, an optically-active dopant is sought so that with very small concentrations of this latter, large values of HTP could be induced.

As such efficient optically-active dopants there are the binaphthol derivatives described in GB-A-2 298 202. However optically-active binaphthol derivatives may undergo partial racemisation when being heated. Besides, their preparation is expensive because it includes asymmetric resolution of binaphthol racemate as a crucial reaction step.

Other classes of optically active dopants which are of easier chemical access than binaphthol derivatives are those described in US-5,780,629, which are consisting of compounds having at least one divalent or polyvalent chiral group and at least one mesogenic group. Based on this molecular architecture, in which the chiral group is present at *peripheral position* of the mesogenic cores, we have prepared some chiral dimesogenic derivatives. Nevertheless, their use as doping agents for liquid crystals has only provided mixtures with a relatively small HTP. However, we have now discovered that a further class of compounds, including within its scope compounds that exhibit a chiral group at *lateral positions* of at least two rod-like shaped organic residues, is efficient for producing a large HTP. Besides, their synthesis is trivial and inexpensive since they are obtained in few reaction steps starting from commercially available optically active residues.

Thus, the invention provides chiral "sandwich" derivatives of formula I:



in which

- 5 A¹ to A⁴ each independently represent hydrogen; an optionally-substituted methyl group; or an optionally-substituted hydrocarbon group of 2 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom, in such a way that oxygen atoms are not linked to one another;
- 10 E¹ and E² each independently represent hydrogen; an optionally-substituted methyl group; or an optionally-substituted hydrocarbon group of 2 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom, in such a way that oxygen atoms are not linked to one another;
- 15 B¹ and B² each independently represent a single bond, an oxygen atom or an optionally-substituted hydrocarbon group of 1 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom, in such a way that oxygen atoms are not linked to one another;
- 20 MG¹ and MG² each independently represent an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms;
- 25 CG is a divalent or polyvalent chiral group derived, in particular, from sugars; from optically active biaryls such as optionally substituted binaphthyl or optionally substituted biphenyl; or from bifunctional or polyfunctional compounds such as optically active alcohols, glycols or amino acids; and
- 30 n₁ and n₂ are each independently 1 or 2, where "n₁ = 2" (or "n₂ = 2") indicates the presence of two separate linkages via the groups B¹ (or the groups B²) between the groups MG¹ and CG (or CG and MG²);

and in which further the substructures $A^1-MG^1-A^2$ and $A^3-MG^2-A^4$ each have a longitudinal axis and are linked lateral to the said longitudinal axis to B^1 and B^2 , respectively.

- 5 One possibility to form a longitudinal axis in the substructures $A^1-MG^1-A^2$ and $A^3-MG^2-A^4$ are compounds where two or more rings or a fused ring system are present in MG^1 or MG^2 . Another possibility are compounds where at least one of A^1 or A^2 and A^3 or A^4 is different from hydrogen.
- 10 The compounds of the present invention are efficient for producing a large HTP.

Their synthesis is trivial and inexpensive since they are obtained in few reaction steps starting from commercially available optically active residues.

- 15 They are compatible with liquid-crystalline compounds or liquid-crystalline mixtures (no significant change of the clearing temperatures when used as dopants in a liquid-crystalline matrix).

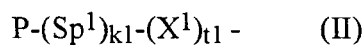
- They induce a large supercooling effect at the liquid-crystalline state when used as dopants in liquid-crystalline matrix hence avoiding crystallisation problems during the manufacture of cholesteric films.
- 20

- They may be used as doping agents for liquid crystals for a wide range of applications including solid state cholesteric filters for projection displays, circular polarisers, optical filters, etc.
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Preferred compounds of the present invention are those belonging to formula (I), in which:

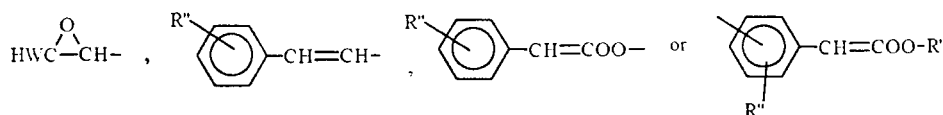
- 30 $n_1 = n_2 = 1.$

Preferably at least one of A¹ to A⁴, E¹ and E² includes a polymerisable group, and each independently may be selected from formula (II):



5 wherein:

P is hydrogen or a polymerisable group selected from groups comprising
 CH₂=CW-, CH₂=W-O-, CH₂=CW-COO-, CH₂=C(Ph)-COO-,
 CH₂=CH-COO-Ph-, CH₂=CW-CO-NH-, CH₂=C(Ph)-CONH-,
 10 CH₂=C(COOR')-CH₂-COO-, CH₂=CH-O-, CH₂=CH-OOC-, (Ph)-CH=CH-,
 CH₃-C=N-(CH₂)_{m3}-, HO-, HS-, HO-(CH₂)_{m3}-, HS-(CH₂)_{m3}-, HO(CH₂)_{m3}COO-,
 HS(CH₂)_{m3}COO-, HWN-, HOC(O)-, CH₂=CH-Ph-(O)_{m4}.



wherein:

15 W represents H, F, Cl, Br or I or a C₁₋₅ alkyl group;

m₃ is an integer having a value of from 1 to 9;

m₄ is an integer having a value of 0 or 1,

R' represents a C₁₋₅ alkyl group; and

R'' represents a C₁₋₅ alkyl group, methoxy, cyano, F, Cl, Br or I;

20

Sp¹ represents an optionally-substituted C₁₋₂₀ alkylene group, in which one or more C-atoms may be replaced by a heteroatom;

k¹ is an integer having a value of from 0 to 4;

25

X¹ represents -O-, -S-, -NH-, N(CH₃)-, -CH(OH)-, -CO-, -CH₂(CO)-, -SO-,
 -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-,
 -SOO-, -OSO-, -SOS-, -CH₂-CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, or -C≡C-; and

t^1 is an integer having a value of 0 or 1.

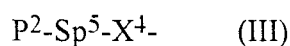
In relation to the residue of formula (II), the term Ph is to be understood as denoting phenylene and (Ph) as denoting phenyl.

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The C_{1-20} alkylene group Sp^1 may comprise branched or straight chain alkylene groups and may be unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN. Alternatively or in addition one or more of CH_2 groups present in the hydrocarbon chain may be replaced, independently, by one or more groups selected from -O-, -S-, -NH-, $N(CH_3)$ -,
 10 -CH(OH)-, -CO-, -CH₂(CO)-, -SO-, -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-,
 -OCO-O-, -S-CO-, -CO-S-, -SOO-, -OSO-, -SOS-, -C≡C-, -(CF₂)_r, -(CD₂)_s or
 C(W¹)=C(W²)-, with the proviso that no two oxygen atoms are directly linked to each
 other. W¹ and W² each represent, independently, H, H-(CH₂)_{q1}- or Cl. The integers r, s
 and q1 each independently represent a number of between 1 and 15.

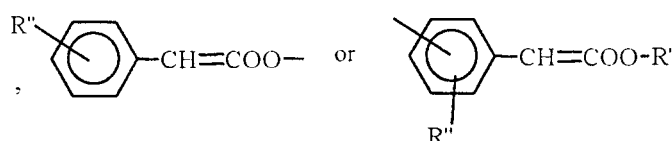
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More preferably, A¹ to A⁴ and E¹ to E² each independently represent a group of formula (III):



20 wherein:

P² represents hydrogen, CH₂=CW⁵- or CH₂=CW⁵-(CO)_{v2}O-,



wherein:

25 W⁵ represents H, CH₃, F, Cl, Br or I; and

v₂ is 0 or 1,

R' represents a C₁₋₅ alkyl group; and

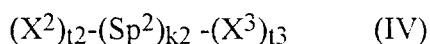
R'' represents a C₁₋₅ alkyl group, methoxy, cyano, F, Cl, Br or I;

Sp⁵ represents a C₁₋₂₀ straight-chain alkylene group, especially ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, or dodecylene; and

- 5 X⁴ represents -O-, -CO-, -COO-, -OCO-, -C≡C-, or a single bond, especially -O-, -COO-, -OCO- or single bond.

One or more of A¹ to A⁴ and E¹ to E² may also represent a C₁-C₂₀-alkyl, C₁-C₂₀-alkoxy, C₁-C₂₀-alkoxycarbonyl, C₁-C₂₀-alkylcarbonyl or C₁-C₂₀-alkylcarbonyl-
 10 oxy group, for example methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, methoxy, ethoxy, *n*-propoxy, isopropoxy, butoxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, pentyloxycarbonyl, hexyloxycarbonyl, octyloxycarbonyl, nonyloxycarbonyl, decyloxycarbonyl, undecyloxy-
 15 carbonyl, dodecyloxycarbonyl, acetyl, propionyl, butyryl, valeryl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, terdecanoyl, acetoxyl, propionyloxy, butyryloxy, valeryloxy, hexanoyloxy, heptanoyloxy, octanoyloxy, nonanoyloxy, decanoyloxy, undecanoyloxy, dodecanoyloxy, terdecanoyloxy and the like.

- 20 In a second preferred embodiment of the present invention each or either of the groups B¹ and/or B² comprises a group of formula (IV):



wherein:

25

Sp² represents a C₁₋₂₀ alkylene group;

X² and X³ each independently represent -O-, -S-, -NH-, N(CH₃)-, -CH(OH)-, -CO-,
 -CH₂(CO)-, -SO-, -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-,
 30 -OCO-O-, -S-CO-, -CO-S-, -SOO-, -OSO-, -SOS-, -CH₂-CH₂-, -OCH₂-,
 -CH₂O-, -CH=CH-, -C≡C- or a single bond;

k^2 is an integer, having a value of 0 or 1; and

t^2 and t^3 are integers, each independently having a value of 0 or 1;

5

with the proviso that oxygen atoms are not linked one to another.

Preferably B^1 and B^2 each independently represent a group of formula (IV), wherein:

10 X^2 to X^3 each independently represent -O-, -CO-, -COO-, -OCO-, -C≡C-, or a single bond, especially -O-, -COO-, -OCO- or a single bond; and

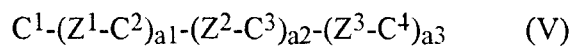
Sp^2 represents a C_{1-20} straight-chain alkylene group, especially ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene,
15 decylene, undecylene or dodecylene.

Especially preferred compounds are those in which B^1 and B^2 each independently represent a group of formula (IV) and A^1 to A^4 and E^1 to E^2 each independently represent a group of formula (III).

20

The invention is particularly useful when the groups of MG^1 and MG^2 have a mesogenic architecture so that compounds of formula (I) are able to be compatible with a host liquid-crystalline single compound or mixture. Thus preferably at least one of MG^1 and MG^2 represents a mesogenic group comprising at least two
25 optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring systems.

Preferably one or more of MG^1 and MG^2 represents a mesogenic group comprising 1 to 4 aromatic or non-aromatic carbocyclic or heterocyclic ring systems and optionally up
30 to 3 bridging groups. These are more preferably selected from the meanings of formulae (V):



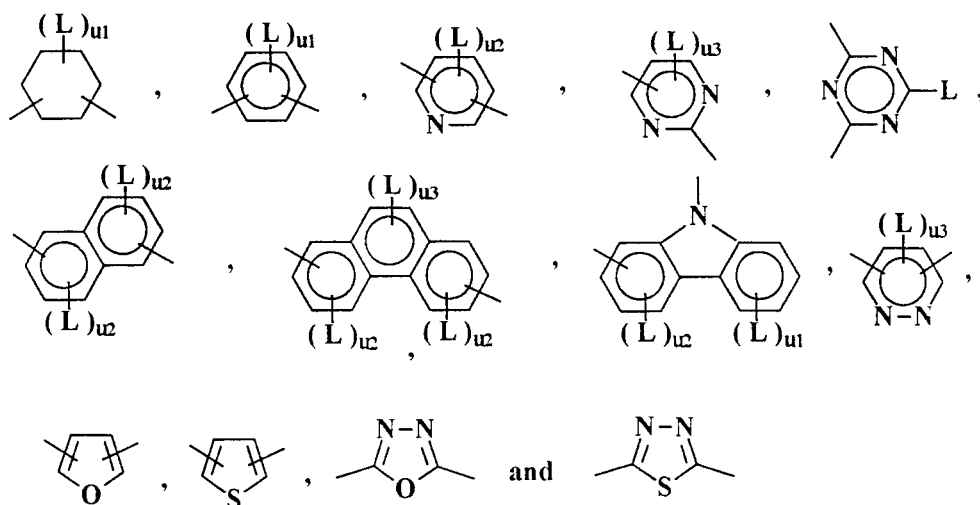
in which:

5 C^1 to C^4 are in each case independently optionally-substituted non-aromatic, aromatic, carbocyclic or heterocyclic groups;

Z^1 to Z^3 are independently from each other $-\text{COO}-$, $-\text{OCO}-$, $-\text{CH}_2\text{-CH}_2-$, $-\text{OCH}_2-$,
 10 $-\text{CH}_2\text{O}-$, $-\text{CH=CH}-$, $-\text{C}\equiv\text{C}-$, $-\text{CH=CH-COO}-$, $-\text{OCO-CH=CH}-$ or a single bond; and

a_1 , a_2 and a_3 are independently integers 0 to 3, such that $a_1 + a_2 + a_3 \leq 3$.

Especially preferred are those in which C^1 to C^4 are selected from:



15

with:

L being $-\text{CH}_3$, $-\text{COCH}_3$, $-\text{NO}_2$, $-\text{CN}$, or halogen

u_1 being 0, 1, 2, 3, or 4,

u_2 being 0, 1, 2, or 3, and

20 u_3 being 0, 1, or 2.

More especially preferred are those in which C¹ to C⁴ are selected from optionally-substituted cyclohexyl or cyclohexylene, phenyl or phenylene, naphthyl or naphthylene or phenanthryl or phenanthrylene.

- 5 For ease of synthesis, the molecules of formula (I) may possess some symmetrical aspects. These include the following possibilities:

$$n_1 = n_2 = 1;$$

10 A¹ to A⁴ are identical;

E¹ and E² are identical;

MG¹ and MG² are identical;

15

CG is a chiral group having at least two chiral centres more preferably two adjacent chiral centres; or

20 B¹ and B² are identical and both consisting of single bonds, oxygen atoms or an optionally-substituted hydrocarbon group of 1 to 3-C atoms.

Other aspects of the present invention are :

25 a) a liquid crystalline material, especially in the form of a liquid crystalline mixture, (co)polymer, elastomer, polymer gel or polymer network, comprising at least two components, at least one of which is a chiral compound, characterised in that the chiral compound is a sandwich derivative of formula (I);

30 b) a liquid crystalline material, especially in the form of a cholesteric mixture, or cholesteric polymer network, comprising at least two components, at least one of which is a chiral compound, characterised in that the chiral compound is a sandwich derivative of formula (I);

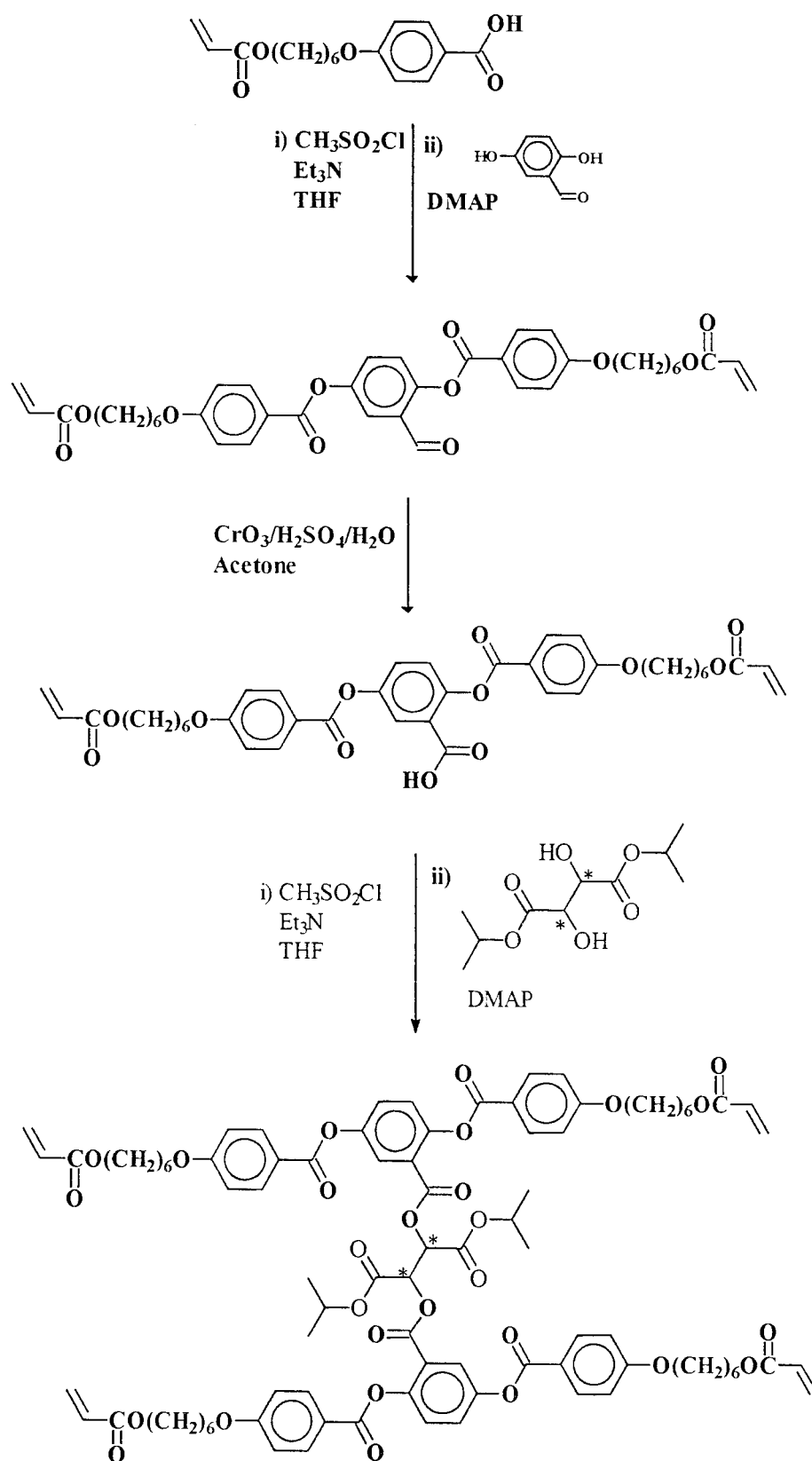
- c) a cholesteric polymer network obtainable by copolymerisation of an optically active polymerisable mesogenic mixture comprising:
- 5 i) at least one chiral or/and achiral nematic polymerisable mixture chosen from the already reported broad range of chiral and achiral nematic materials, for example as in *Adv. Mater.* **5**, 107 (1993), *Mol. Cryst. Liq. Cryst.* **307**, 111 (1997), *J. Mat. Chem.* **5**, 2047 (1995) or in patent publications US 5593617; US 5567349; GB-A-2297556; GB-A-2299333; DE-A-19504224; EP-A-0606940; EP-A-0643121 and EP-A-0606939, optionally selected
10 from EP-A-0606940; EP-A-0643121 and EP-A-0606939;
 - ii) at least one chiral dopant of formula (I);
 - iii) an initiator;
15
 - iv) optionally a non-mesogenic compound having at least one polymerisable functional group, more optionally a diacrylate compound; and
 - v) optionally a stabiliser;
20
- d) chiral polymerisable cholesteric mixtures, essentially consisting of:
- 25 i) 70 to 99 %, preferably 85 to 95 % by weight of at least one achiral polymerisable liquid crystal;
 - ii) 0.1 to 30 %, preferably 1 to 15 % by weight of a chiral compound of formula I;
 - iii) 0.1 to 5 %, preferably 0.2 to 2 % by weight of a photoinitiator; and
30
 - iv) 0 to 5 %, preferably 0.1 to 1 % of a stabiliser; and

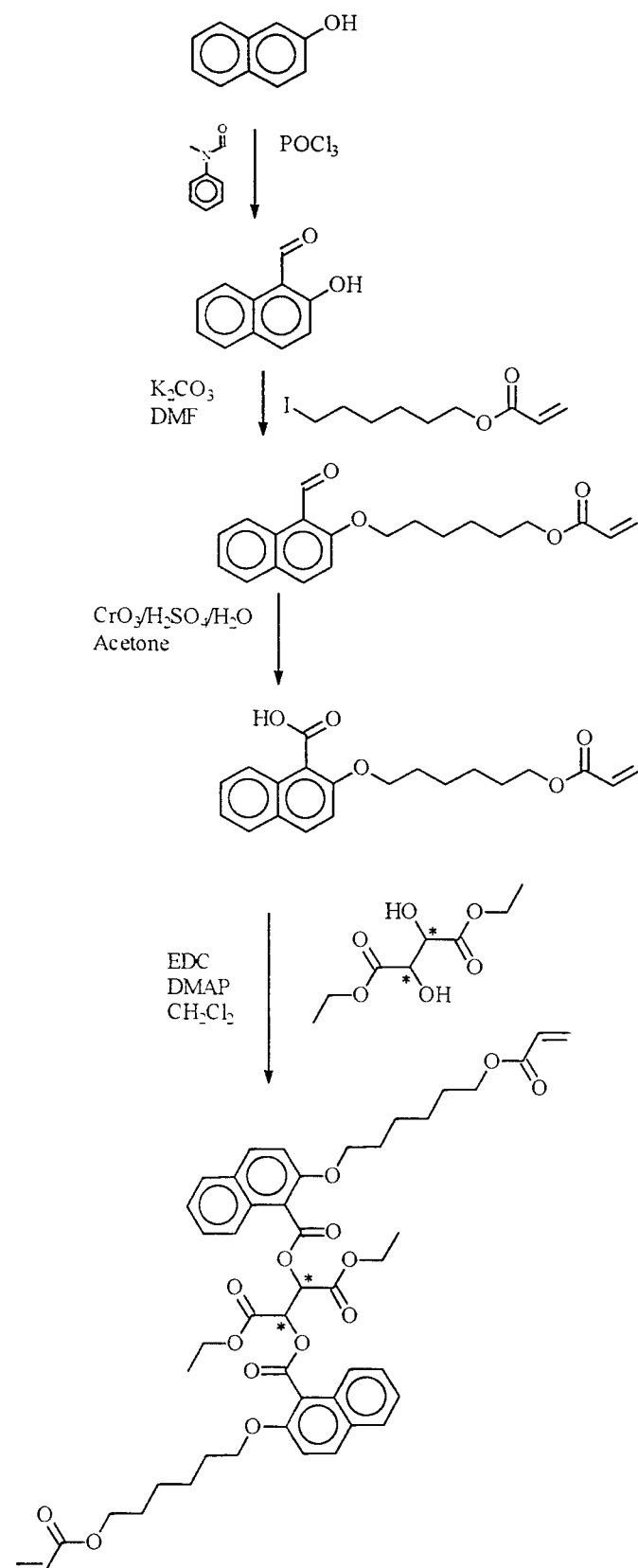
- e) a cholesteric film obtainable by the steps comprising ordering the above mixture in the monomeric state and *in situ* UV polymerisation of the resulting ordered mixture.

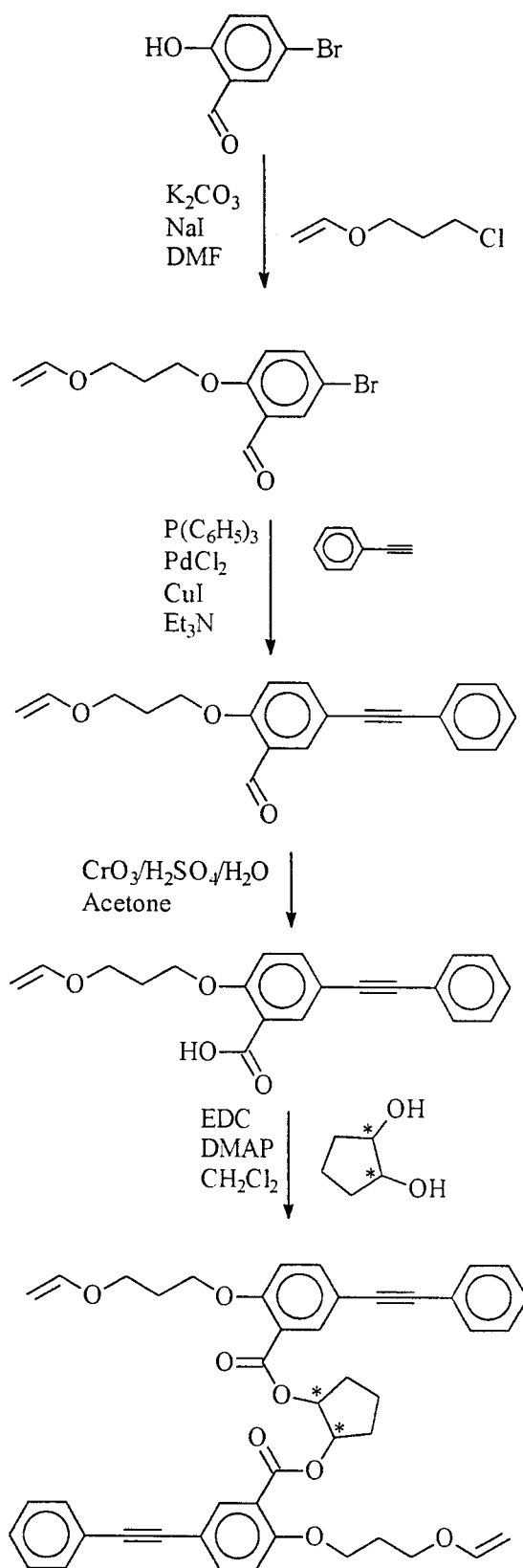
5 The invention also includes:

- a) the use of the compounds as dopants for liquid crystals;
- b) the use of the compounds or liquid crystalline materials for manufacturing a
10 polymeric cholesteric layer; and
- c) the use of the cholesteric polymer network, chiral polymerisable cholesteric mixtures, or cholesteric film, in optical components such as optical filters and polarisers, and especially colour filters, optical pass band filters, solid state
15 cholesteric filters for projection displays and circular polarisers.

The compounds of the invention may be readily prepared using methods that are well known to the person skilled in the art, such as those documented in Houben-Weyl, *Methoden der Organischen Chemie*, Thieme-Verlag, Stuttgart. The compounds may for
20 example be made according to the following reaction schemes:

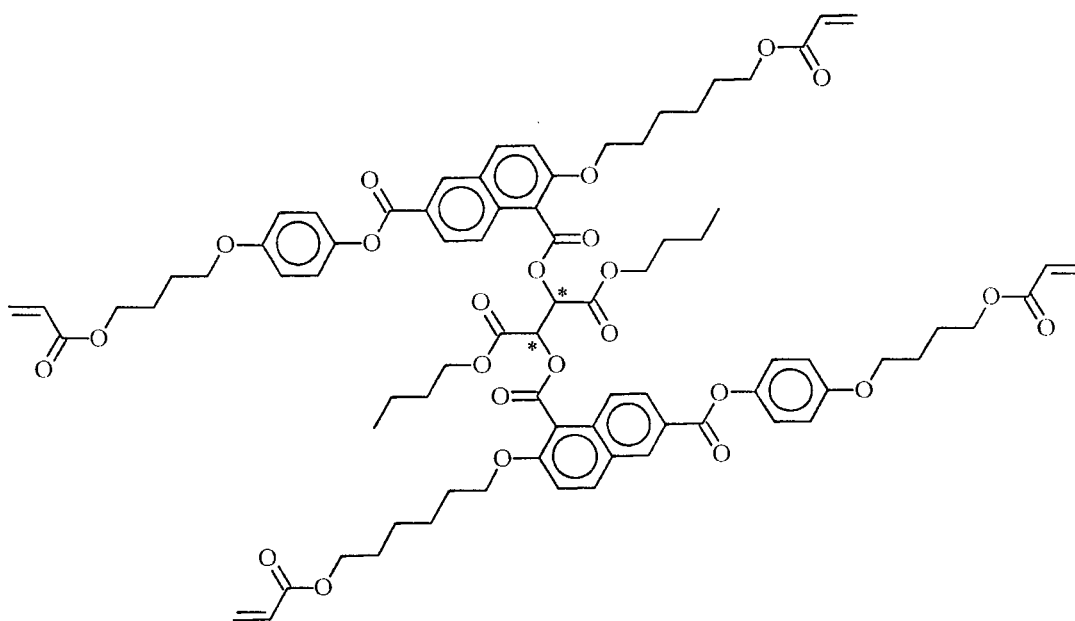
Scheme 1:

Scheme 2:

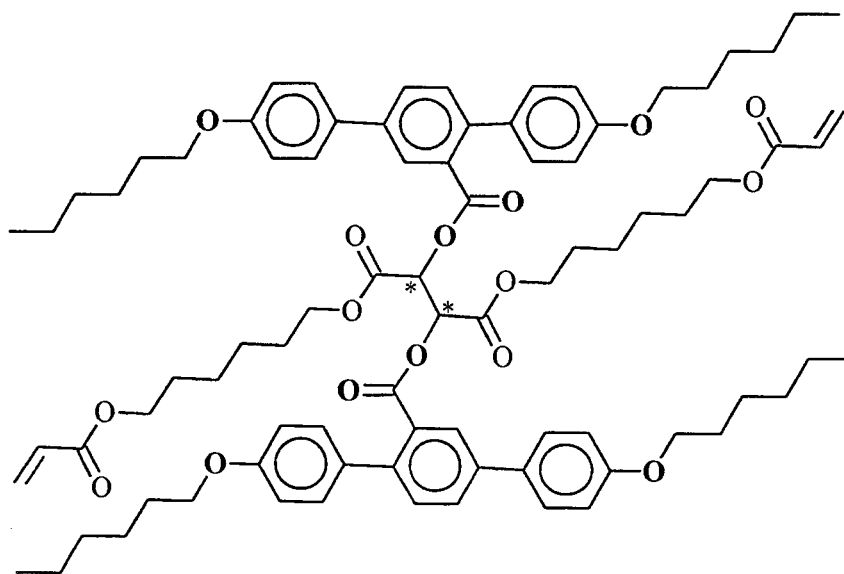
Scheme 3:

EDC : *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride; DMAP: *N,N*-Dimethylaminopyridine; DMF: *N,N*-Dimethylformamide

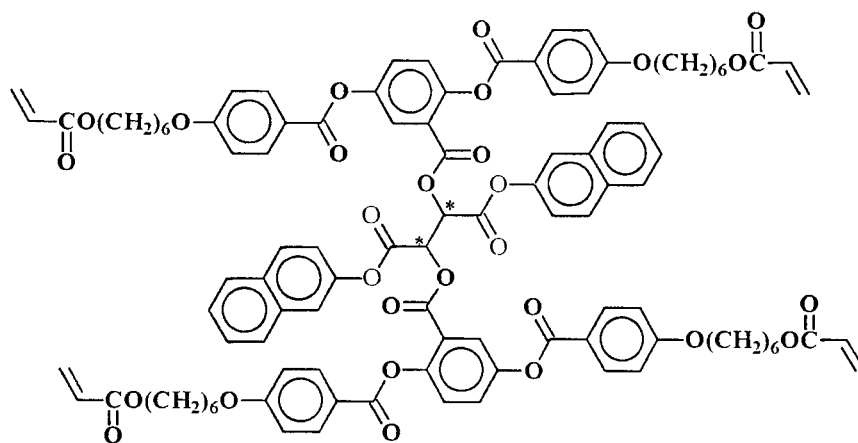
According to the synthetic ways drawn in Schemes 1-3 typical examples
5 representing polymerisable chiral "sandwich" derivatives shown in the following list of
compounds are prepared. This list is, however, to be understood only as illustrative
without limiting the scope of the present invention:



E. 1

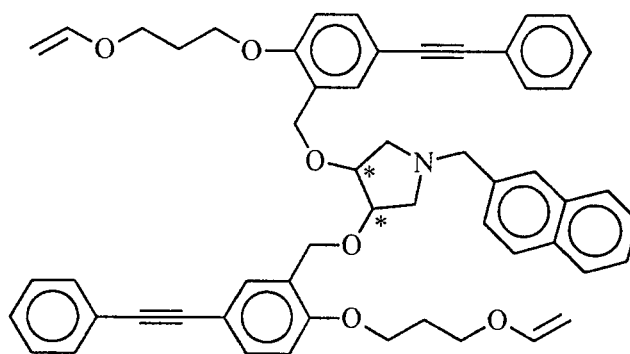


E. 2

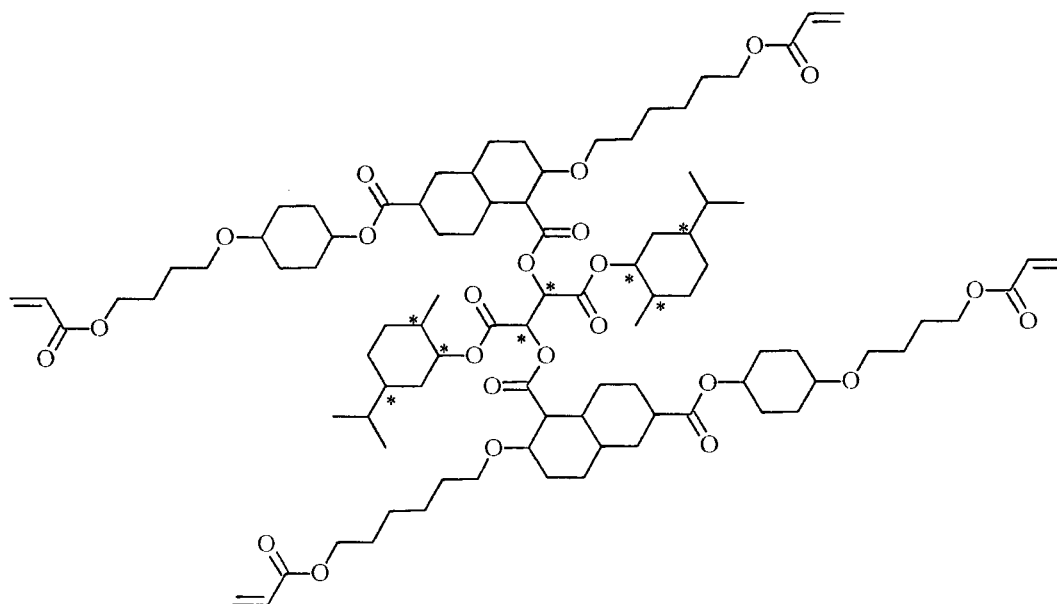


E. 3

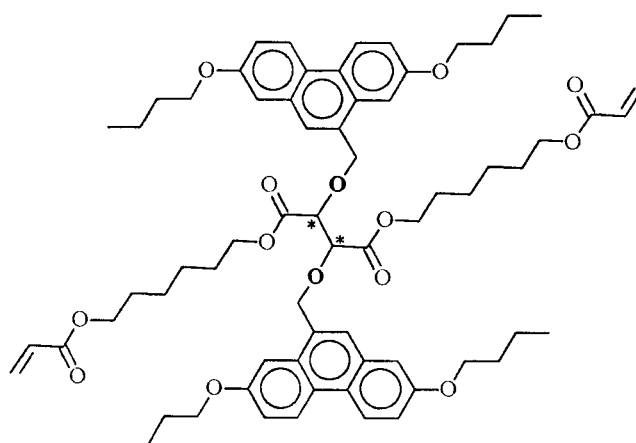
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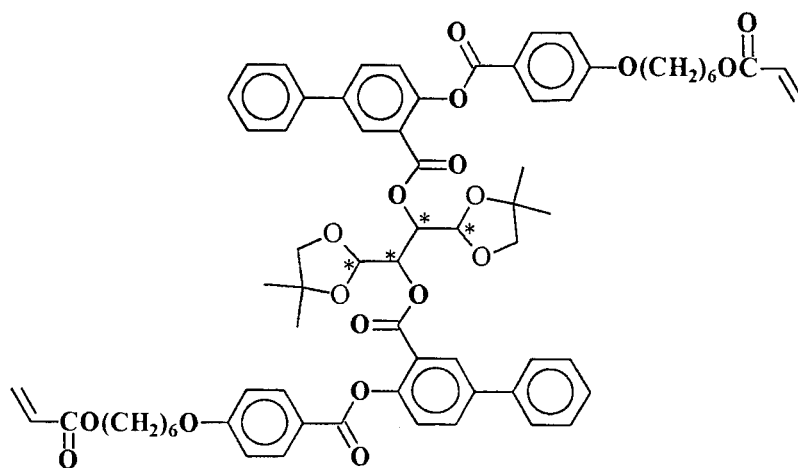
E. 4



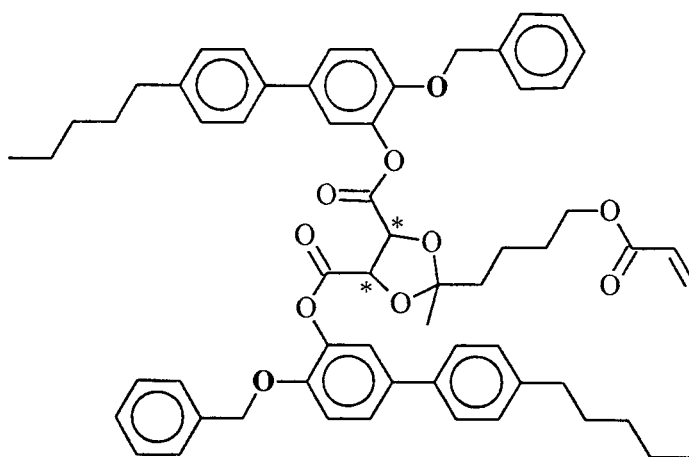
E. 5



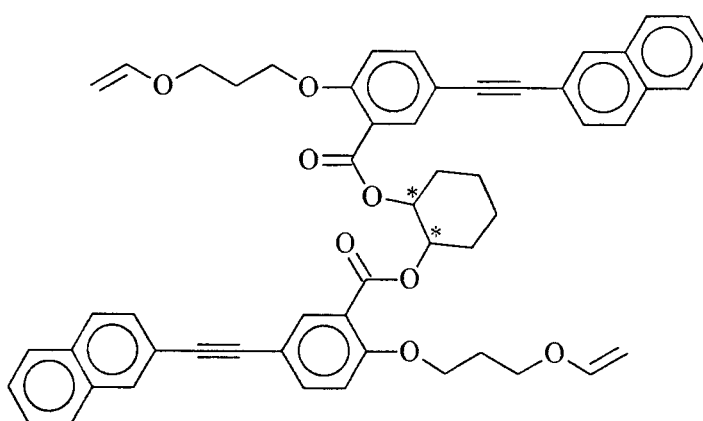
E. 6



E. 7



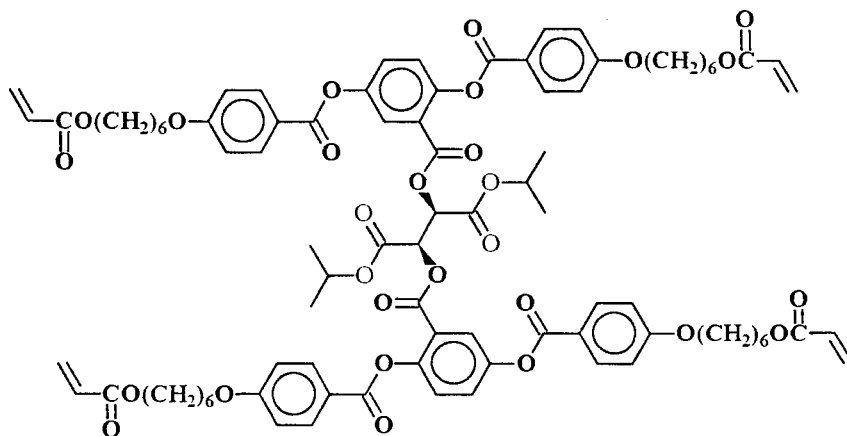
E. 8



E. 9

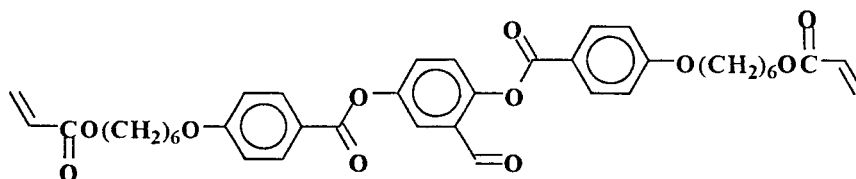
Example 1:

Diisopropyl L-2,3-bis-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}-succinate



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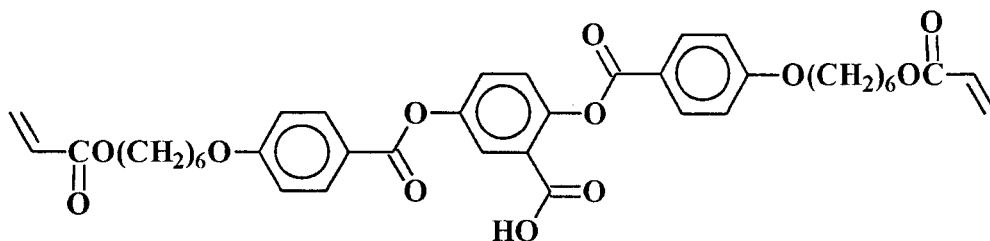
a) *2,5-Di-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzaldehyde*



A solution of mesyl chloride (4.23 g, 36.94 mmol) in 10 ml of dry THF was added dropwise under argon over a period of 15 minutes to a cooled (-25 °C) solution of 4-(6-acryloyloxyhexyloxy)benzoic acid and triethylamine (20 ml) in 80 ml of dry THF. The reaction mixture was then stirred for 60 min at -25 °C, treated with a solution of 2,5-dihydroxybenzaldehyde (2.3 g, 16.65 mmol) in 60 ml of dry THF containing 195 mg of DMAP and further stirred at -25°C for 2h. The reaction mixture was then allowed to warm to room temperature and stirring was continued overnight. The reaction mixture was then poured into 120 ml of saturated NaHCO₃ and extracted with 2 x 200 ml of ether. The combined organic extracts were washed with 3N HCl (200 ml) and semi-saturated NaCl solution (2 x 100 ml), dried over MgSO₄, filtered and dried to give a slightly yellow pasty material. This was purified by flash chromatography over a short silica column (CH₂Cl₂/Et₂O : 19.5 / 0.5) to give a white residue (9.25 g) which was dissolved in CH₂Cl₂ (25 ml) then recrystallised from ethanol (250 ml) to give pure

2,5-di-[4-(6-acryloyloxy-hexyloxy)benzoyloxy]benzaldehyde as a white crystalline material. Yield 8.5 g.

b) 2,5-Di-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid



5

Jones oxidant ($\text{CrO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$) (48 ml) was added to a ice-cooled solution of 2,5-di-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzaldehyde (8.24 g, 12 mmol) in acetone (300 ml) in a dropwise fashion over a period of 30 min. The reaction mixture was stirred overnight at room temperature. The resulting green-orange mixture was filtered off to leave a green precipitate that was washed with 600 ml of ether. The combined organic solutions were washed with water until the orange coloration disappeared (6 x 250 ml). The colourless organic solution obtained was washed with saturated NaCl solution (2 x 300 ml), dried over MgSO_4 and filtered. Removal of the solvent gave pure 2,5-di-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid as a white crystalline material. Yield 8.5 g.

15

c) Diisopropyl L-2,3-bis-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}succinate

A solution of mesyl chloride (1.10 ml) in 5 ml of dry THF is dropwise added to a solution of 2',5'-bis-[2,5-di-(4-(6-acryloyloxyhexyloxy)benzoyloxy)]benzoic acid (10 g) and triethylamine (19.8 ml) in 125 ml of dry THF, cooled at -25°C and maintained and under argon atmosphere. After complete addition (15 min), the reaction mixture is further stirred for 120 min at -25°C then treated with a solution of diisopropyl L-tartrate (1.35 g) in 20 ml of dry THF containing 695 mg of DMAP and the reaction mixture is further stirred at -25°C for 2 h. The temperature is then allowed to reach room temperature and stirring is continued overnight. The reaction mixture is filtered over Celite and evaporated to dryness to afford a slightly beige pasty material. This is then

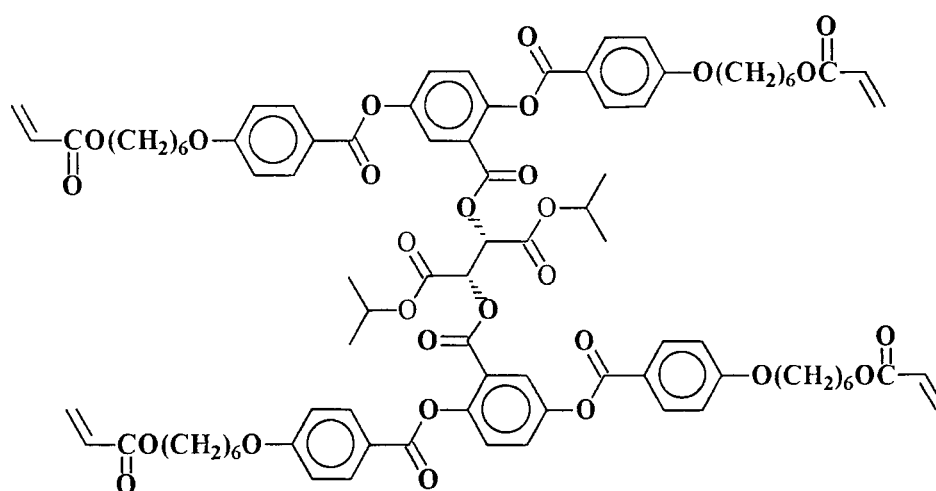
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flash chromatographed over a silica column affording pure diisopropyl L-2,3-bis-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}succinate [the "L" indicating the formal derivation of the compound from diisopropyl L-tartrate] as a transparent oily material which becomes pasty upon standing.

5 Yield: 5.0 g.

Example 2:

10 *Diisopropyl D-2,3-bis-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}-succinate*

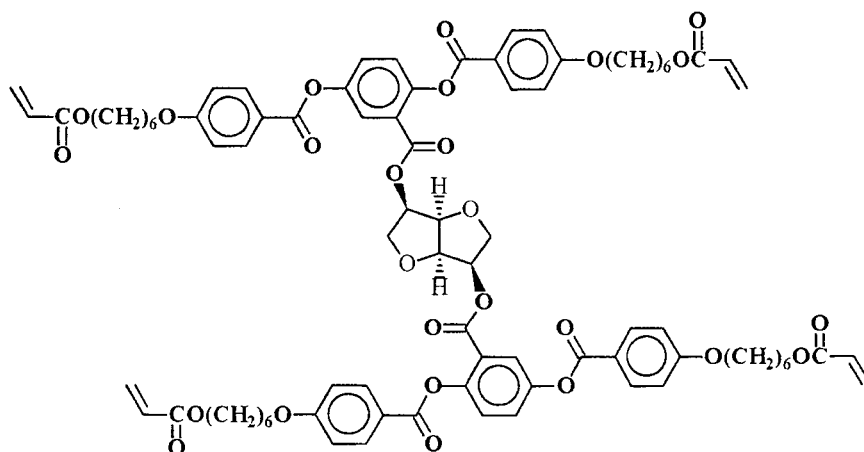


Following the procedure described in Example 1 (C), the reaction was performed with 10 g of 2',5'-bis-[2,5-di-(4-(6-acryloyloxyhexyloxy)benzoyloxy)]benzoic acid, 1.10 ml of mesyl chloride, 19.8 ml of triethylamine, 1.5 g of diisopropyl L-tartrate and 695 mg of DMAP to afford, after flash chromatography over a silica column, pure diisopropyl D-2,3-bis-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxysuccinate [the "D" indicating the formal derivation of the compound from diisopropyl D-tartrate] as a transparent oily material which becomes pasty upon standing.

20 Yield: 6.3 g.

Example 3:

O,O-Di-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyl}-1,4,3,6-dianhydro-D-mannitol



5

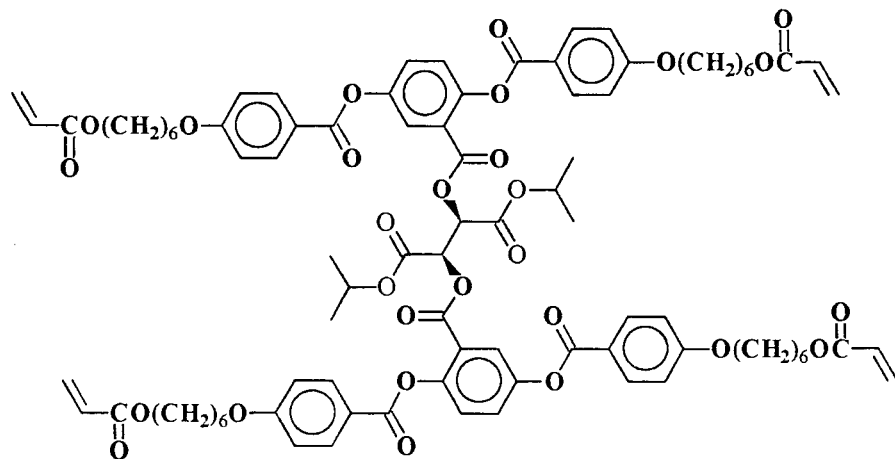
Following the procedure described in Example 1 (C), the reaction was performed with 1.5 g of 2',5'-bis-[2,5-di-(4-(6-acryloyloxyhexyloxy)benzoyloxy)]benzoic acid, 0.17 ml of mesyl chloride, 3 ml of triethylamine, 0.14 g of 1,4,3,6-dianhydro-D-mannitol and 61 mg of DMAP in 50 ml of THF to afford, after flash chromatography over a silica column, pure *O,O*-di-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyl}-1,4,3,6-dianhydro-D-mannitol as white crystalline material.

Yield: 0.28 g.

Example 4:

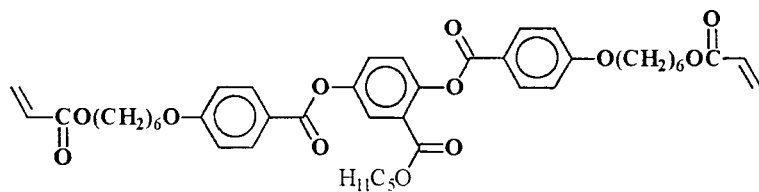
A mixture is formulated consisting of

5 1 % by weight of



and

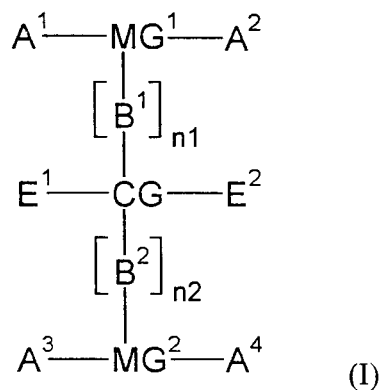
10 99 % by weight of



This mixture forms a cholesteric phase with a pitch of $p = 4 \mu\text{m}$.

Claims

1. A compound of formula I:



5

in which:

- A¹ to A⁴ each independently represent hydrogen; an optionally-substituted methyl group; or an optionally-substituted hydrocarbon group of 2 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom, in such a way that oxygen atoms are not linked to one another;
- E¹ and E² each independently represent hydrogen; an optionally-substituted methyl group; or an optionally-substituted hydrocarbon group of 2 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom, in such a way that oxygen atoms are not linked to one another;
- B¹ and B² each independently represent a single bond, an oxygen atom or an optionally-substituted hydrocarbon group of 1 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom, in such a way that oxygen atoms are not linked to one another;

MG¹ and MG² each independently represent an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms;

5 CG is a divalent or polyvalent chiral group; and

n₁ and n₂ are each independently 1 or 2, where "n₁ = 2" (or "n₂ = 2") indicates the presence of two separate linkages via the groups B¹ (or the groups B²) between the groups MG¹ and CG (or CG and MG²);

10

and in which further the substructures A¹-MG¹-A² and A³-MG²-A⁴ each have a longitudinal axis and are linked lateral to the said longitudinal axis to B¹ and B², respectively.

15 2. A compound as claimed in claim 1, in which CG is a chiral group derived from a sugar, from an optically active biaryl group, or from a bifunctional or polyfunctional compound comprising an optically active alcohol, glycol or amino acid.

3. A compound as claimed in claim 1 or 2 in which:

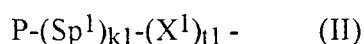
20

$$n_1 = n_2 = 1$$

4. A compound as claimed in any preceding claim, in which at least one of A¹ to A⁴, E¹ and E² includes a polymerisable group.

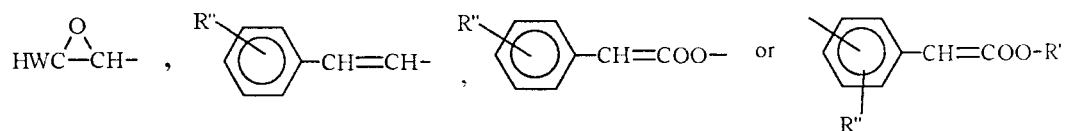
25

5. A compound as claimed in claim 4, in which at least one of A¹ to A⁴, E¹ and E² independently is selected from formula (II):



30 wherein:

- P is hydrogen or a polymerisable group selected from groups comprising
 $\text{CH}_2=\text{CW}-$, $\text{CH}_2=\text{CW}-\text{O}-$, $\text{CH}_2=\text{CW}-\text{COO}-$, $\text{CH}_2=\text{C}(\text{Ph})-\text{COO}-$,
 $\text{CH}_2=\text{CH}-\text{COO}-\text{Ph}-$, $\text{CH}_2=\text{CW}-\text{CO}-\text{NH}-$, $\text{CH}_2=\text{C}(\text{Ph})-\text{CONH}-$,
 $\text{CH}_2=\text{C}(\text{COOR}')-\text{CH}_2-\text{COO}-$, $\text{CH}_2=\text{CH}-\text{O}-$, $\text{CH}_2=\text{CH}-\text{OOC}-$, $(\text{Ph})-\text{CH}=\text{CH}-$,
 5 $\text{CH}_3-\text{C}=\text{N}-(\text{CH}_2)_{m3}-$, $\text{HO}-$, $\text{HS}-$, $\text{HO}-(\text{CH}_2)_{m3}-$, $\text{HS}-(\text{CH}_2)_{m3}-$, $\text{HO}(\text{CH}_2)_{m3}\text{COO}-$,
 $\text{HS}(\text{CH}_2)_{m3}\text{COO}-$, $\text{HWN}-$, $\text{HOC}(\text{O})-$, $\text{CH}_2=\text{CH}-\text{Ph}-(\text{O})_{m4}$.



wherein:

- W represents H, F, Cl, Br or I or a C_{1-5} alkyl group;
 10 $m3$ is an integer having a value of from 1 to 9;
 $m4$ is an integer having a value of 0 or 1,
 R' represents a C_{1-5} alkyl group; and
 R'' represents a C_{1-5} alkyl group, methoxy, cyano, F, Cl, Br or I;
 15 Sp^1 represents an optionally-substituted C_{1-20} alkylene group, in which one or more
 C-atoms may be replaced by a heteroatom;
 k^1 is an integer having a value of from 0 to 4;
 20 X^1 represents $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $\text{N}(\text{CH}_3)-$, $-\text{CH}(\text{OH})-$, $-\text{CO}-$, $-\text{CH}_2(\text{CO})-$, $-\text{SO}-$,
 $-\text{CH}_2(\text{SO})-$, $-\text{SO}_2-$, $-\text{CH}_2(\text{SO}_2)-$, $-\text{COO}-$, $-\text{OCO}-$, $-\text{OCO}-\text{O}-$, $-\text{S}-\text{CO}-$, $-\text{CO}-\text{S}-$,
 $-\text{SOO}-$, $-\text{OSO}-$, $-\text{SOS}-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{OCH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}=\text{CH}-$, or $-\text{C}\equiv\text{C}-$; and
 t^1 is an integer having a value of 0 or 1;

25

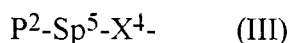
wherein the term Ph denotes phenylene and (Ph) denotes phenyl.

6. A compound as claimed in claim 5, in which one or more of CH_2 groups present
 in the hydrocarbon chain of an the optionally-substituted C_{1-20} alkylene group Sp^1 is

replaced, independently, by one or more groups selected from -O-, -S-, -NH-, N(CH₃)-, -CH(OH)-, -CO-, -CH₂(CO)-, -SO-, -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -SOO-, -OSO-, -SOS-, -C≡C-, -(CF₂)_r, -(CD₂)_s or C(W¹)=C(W²)-, with the proviso that no two oxygen atoms are directly linked to each other, wherein W¹ and W² each represent, independently, H, H-(CH₂)_{q1}- or Cl and the integers r, s and q1 each independently represent a number of between 1 and 15.

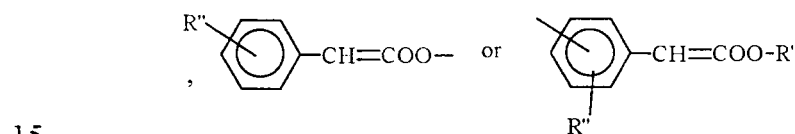
7. A compound as claimed in any preceding claim, in which A¹ to A⁴ and E¹ to E² each independently represent a group of formula (III):

10



wherein:

P² represents hydrogen, CH₂=CW⁵- or CH₂=CW⁵-(CO)_{v2}O-,



15

wherein:

W⁵ represents H, CH₃, F, Cl, Br or I; and

v₂ is 0 or 1,

R' represents a C₁₋₅ alkyl group; and

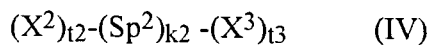
20 R'' represents a C₁₋₅ alkyl group, methoxy, cyano, F, Cl, Br or I,

Sp⁵ represents a C₁₋₂₀ straight-chain alkylene group, especially ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, or dodecylene; and

25

X⁴ represents -O-, -CO-, -COO-, -OCO-, -C≡C-, or a single bond, especially -O-, -COO-, -OCO- or single bond.

8. A compound as claimed in any preceding claim, in which each or either of the groups B¹ and/or B² comprises a group of formula (IV):



5 wherein:

Sp² represents a C₁₋₂₀ alkylene group;

10 X² and X³ each independently represent -O-, -S-, -NH-, N(CH₃)-, -CH(OH)-, -CO-,
-CH₂(CO)-, -SO-, -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-,
-OCO-O-, -S-CO-, -CO-S-, -SOO-, -OSO-, -SOS-, -CH₂-CH₂-, -OCH₂-,
-CH₂O-, -CH=CH-, -C≡C- or a single bond;

k² is an integer, having a value of 0 or 1; and

15

t² and t³ are integers, each independently having a value of 0 or 1;

with the proviso that oxygen atoms are not linked one to another.

20 9. A compound as claimed in claim 8, in which B¹ and B² each independently represent a group of formula (IV), wherein:

X² to X³ each independently represent -O-, -CO-, -COO-, -OCO-, -C≡C-, or a single bond, especially -O-, -COO-, -OCO- or a single bond; and

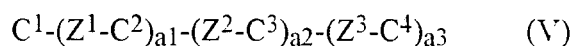
25

Sp² represents a C₁₋₂₀ straight-chain alkylene group, especially ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene or dodecylene.

10. A compound as claimed in any preceding claim, in which at least one of MG^1 and MG^2 represents a mesogenic group comprising at least two optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring systems.

5 11. A compound as claimed in any preceding claim, in which one or more of MG^1 and MG^2 represents a mesogenic group comprising 1 to 4 aromatic or non-aromatic carbocyclic or heterocyclic ring systems and optionally up to 3 bridging groups.

10 12. A compound as claimed in claim 11, in which MG^1 and MG^2 are selected from the meanings of formulae (V):



in which:

15

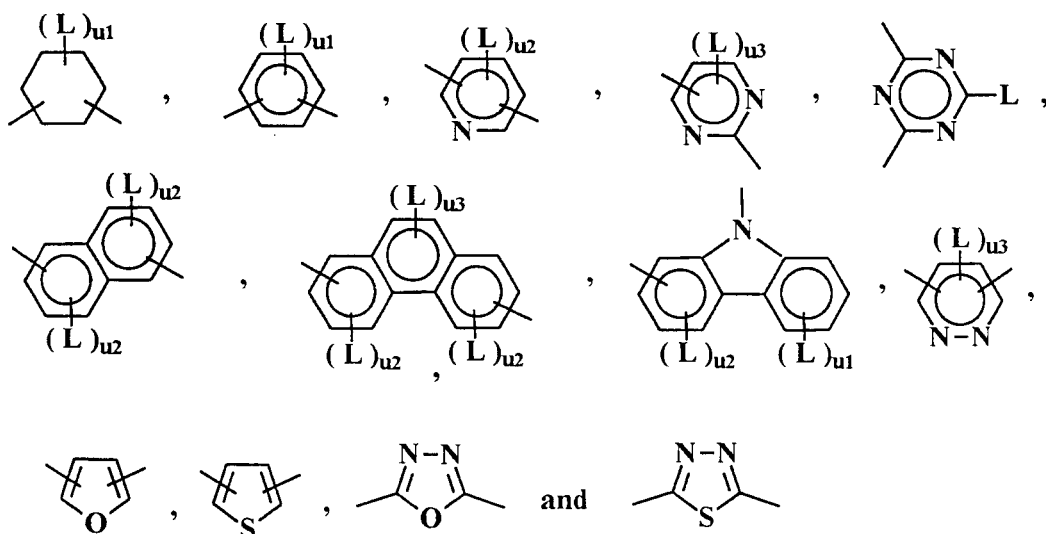
C^1 to C^4 are in each case independently optionally-substituted non-aromatic, aromatic, carbocyclic or heterocyclic groups;

20

Z^1 to Z^3 are independently from each other $-COO-$, $-OCO-$, $-CH_2-CH_2-$, $-OCH_2-$, $-CH_2O-$, $-CH=CH-$, $-C\equiv C-$, $-CH=CH-COO-$, $-OCO-CH=CH-$ or a single bond; and

a_1 , a_2 and a_3 are independently integers 0 to 3, such that $a_1 + a_2 + a_3 \leq 3$.

13. A compound as claimed in claim 12, in which C^1 to C^4 are selected from:



with:

L being $-CH_3$, $-COCH_3$, $-NO_2$, $-CN$, or halogen

- 5 u1 being 0, 1, 2, 3, or 4,
 u2 being 0, 1, 2, or 3, and
 u3 being 0, 1, or 2.

14. A compound as claimed in claim 13, in which C^1 to C^4 are selected from
 10 optionally-substituted cyclohexyl or cyclohexylene, phenyl or phenylene, naphthyl or naphthylene or phenanthryl or phenanthrylene.

15. A compound as claimed in any preceding claim, in which A^1 to A^4 are identical.

15 16. A compound as claimed in any preceding claim, in which E^1 and E^2 are identical.

17. A compound as claimed in any preceding claim, in which MG^1 and MG^2 are identical.

20

18. A compound as claimed in any preceding claim, in which CG is a chiral group having at least two chiral centres more preferably two adjacent chiral centres.

19. A compound as claimed in any preceding claim, in which B¹ and B² are identical and both consisting of single bonds, oxygen atoms or an optionally-substituted hydrocarbon group of 1 to 3-C atoms.

5

20. A liquid crystalline material, in the form of a liquid crystalline mixture, (co)polymer, elastomer, polymer gel or polymer network, comprising at least two components, at least one of which is a chiral compound, characterised in that the chiral compound is a compound of formula (I) as claimed in claim 1.

10

21. A liquid crystalline material, in the form of a cholesteric mixture, or cholesteric polymer network, comprising at least two components, at least one of which is a chiral compound, characterised in that the chiral compound is a compound of formula (I) as claimed in claim 1.

15

22. A cholesteric polymer network obtainable by copolymerisation of an optically active polymerisable mesogenic mixture comprising:

20 i) at least one chiral or/and achiral nematic polymerisable mixture chosen from chiral and achiral nematic materials;

ii) at least one chiral dopant of formula (I) as claimed in claim 1;

iii) an initiator;

25

iv) optionally a non-mesogenic compound having at least one polymerisable functional group, more optionally a diacrylate compound; and

v) optionally a stabiliser;

30

23. A chiral polymerisable cholesteric mixture, essentially consisting of:
- i) 70 to 99 % by weight of at least one achiral polymerisable liquid crystal;
 - 5 ii) 0.1 to 30 % by weight of a chiral compound of formula I as claimed in claim 1;
 - iii) 0.1 to 5 % by weight of a photoinitiator; and
 - 10 iv) 0 to 5 % of a stabiliser.
24. A cholesteric film obtainable by the steps comprising ordering a chiral polymerisable cholesteric mixture as claimed in claim 23 in the monomeric state and *in situ* UV polymerisation of the resulting ordered mixture.
- 15 25. Use of a compound as claimed in any one of claims 1 to 19 as a dopant for liquid crystals.
26. Use of a compound as claimed in any one of claims 1 to 19, or a liquid crystalline material as claimed in claim 20 or 21, for manufacturing a polymeric cholesteric layer.
- 20 27. Use of a cholesteric polymer network as claimed in claim 22, a chiral polymerisable cholesteric mixture as claimed in claim 23, or a cholesteric film as claimed in claim 24, in optical components such as colour filters, optical pass band filters and polarisers.
- 25