

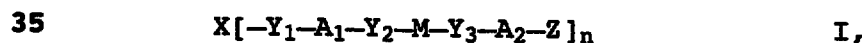
Polymerizable oligomesogens

5 It is known that media which are anisotropic in shape can form liquid-crystalline phases, known as mesophases, on warming. The individual phases differ through the spatial arrangement of the major parts of the molecules on the one hand and through the molecular arrangement with respect to the long axes on the other hand (G.W. Gray, P.A. Winsor, *Liquid Crystals and Plastic*
 10 *Crystals*, Ellis Horwood Limited, Chichester, 1974). The nematic liquid-crystalline phase is distinguished by the fact that there is only one alignment long-distance ordering due to the long molecular axes lining up in parallel. Under the prerequisite that the molecules making up the nematic phase are chiral, a
 15 cholesteric phase forms, in which the long axes of the molecules form a helical superstructure perpendicular thereto (H. Baessler, *Festkörperprobleme XI*, 1971). The chiral moiety may be present either in the liquid-crystalline molecule itself or added to the nematic phase as a dope inducing the cholesteric phase. This
 20 phenomenon was first studied on cholesterol derivatives (eg. H. Baessler, M.M. Labes, *J. Chem. Phys.* 52 (1970) 631; H. Baessler, T.M. Laronge, M.M. Labes, *J. Chem. Phys.* 51 (1969) 3213; H. Finkelmann, H. Stegemeyer, *Z. Naturforschg.* 28a (1973) 799; H. Stegemeyer, K.J. Mainusch, *Naturwiss.* 58 (1971) 599; H.
 25 Finkelmann, H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.* 78 (1974) 869).

The cholesteric phase has remarkable optical properties: large
 30 optical rotation and pronounced circular dichroism caused by selective reflection of circular-polarized light within the cholesteric layer. The different colors to be observed depending on the viewing angle depend on the pitch of the helical superstructure, which is itself dependent on the twisting power
 35 of the chiral component. The pitch and thus the wavelength range of the selectively reflected light of a cholesteric layer can be varied, in particular, by changing the concentration of a chiral dope. Such cholesteric systems offer interesting opportunities for practical use. Thus, incorporation of chiral moieties into
 40 mesogenic acrylic esters and alignment in the cholesteric phase, for example after photocrosslinking, can give a stable, colored network, but the concentration of the chiral component therein cannot be changed (G. Galli, M. Laus, A. Angeloni, *Makromol. Chem.* 187 (1986) 289). Admixing of non-crosslinkable, chiral
 45 compounds with nematic acrylic esters can give by photocrosslinking a colored polymer which still contains high proportions of soluble components (I. Heyndricks, D.J. Broer, *Mol. Cryst. Liq.*

- Cryst. 203 (1991) 113). Furthermore, random hydrosilylation of mixtures of cholesterol derivatives and acrylate-containing mesogens using defined cyclic siloxanes followed by photopolymerization allows the production of a cholesteric network in which the chiral component can comprise up to 50 % of the material employed; however these polymers also contain significant amounts of soluble components (F.H. Kreuzer, R. Maurer, C. Müller-Rees, J. Stohrer, Paper No. 7, 22nd Freiburg Congress on Liquid Crystals, Freiburg 1993).
- DE-A-35 35 547 describes a process in which a mixture of cholesterol-containing monoacrylates can be converted into cholesteric layers by photocrosslinking. However, the total proportion of the chiral component in the mixture is about 94 %.
- Although a material of this type is not very mechanically stable as a pure side-chain polymer, an increase in the stability can, however, be achieved by means of highly crosslinking diluants.
- In addition to the nematic and cholesteric networks described above, smectic networks are also known; these are prepared, in particular, by photopolymerization/photocrosslinking of smectic liquid-crystalline materials in the smectic liquid-crystalline phase. The materials used for this purpose are generally symmetrical liquid-crystalline bisacrylates, as described, for example, by D.J. Broer and R.A.M. Hikmet, Makromol. Chem., 190, (1989), 3201-3215. However, these materials have very high clearing points of > 120°C, with the associated risk of thermal polymerization. If an S_c phase exists, piezoelectric properties can be achieved by admixing chiral materials (R.A.M. Hikmet, Macromolecules 25, (1992), p. 5759).

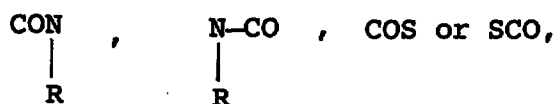
The present invention relates to structures of the formula I



where

- X is a silicon-free, n-valent central unit, the radicals
- A₁ and A₂, independently of one another, are a direct bond or a spacer, the radicals
- Y₁, Y₂ and Y₃, independently of one another, are a direct bond, O, S, CO, OCO, COO, OCOO,

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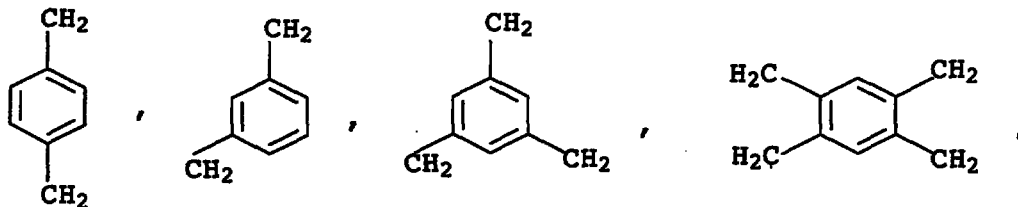
M is a mesogenic group,

Z is a polymerizable group, and

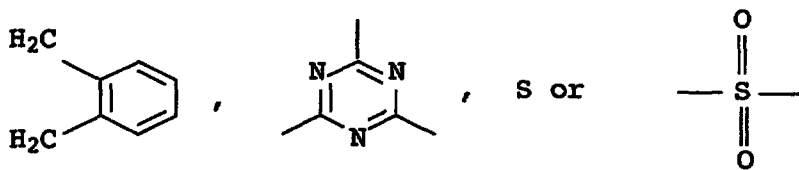
10 n is a number from 2 to 6, where

R is hydrogen, or C₁- to C₄-alkyl, and the combination of M-Y₃ A₂-Z can be a cholesteryl radical.15 The radicals X can be aliphatic, aromatic or cycloaliphatic and may additionally contain heteroatoms. Also suitable are divalent elements and groups such as O, S, SO₂ and CO.20 X can be, in particular, C₂- to C₁₂- alkylene, -alkenylene or -alkynylene radicals, which may be interrupted by one or more O or S atoms or NR groups, or phenylene, benzylene or cyclohexylene or radicals of the formula

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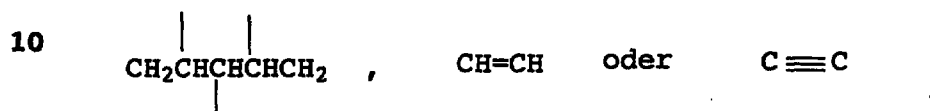
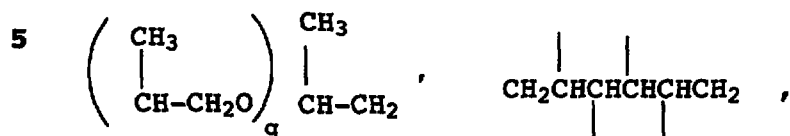
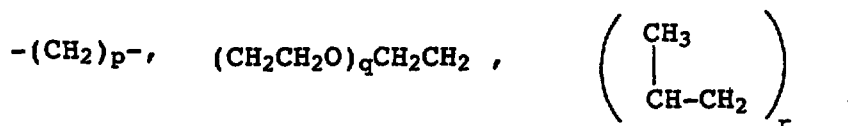
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Examples of individual alkylene, alkenylene or alkynylene radicals are,

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where

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p is a number from 2 to 12,

q is a number from 1 to 3 and

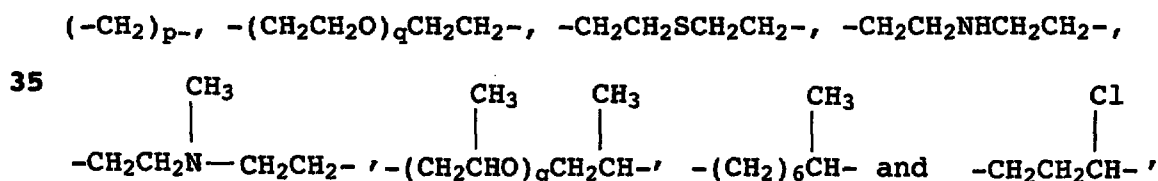
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r is a number from 1 to 6.

Suitable spacers are all groups which are known for this purpose; the spacers are usually linked to X via ester or ether groups or
25 a direct bond. The spacers generally contain from 2 to 30, preferably from 2 to 12, in particular from 6 to 12, carbon atoms and may be interrupted in the chain, for example by O, S, NH or NCH₃. Suitable substituents for the spacer chain are fluorine, chlorine, bromine, cyano, methyl or ethyl.

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Examples of representative spacers are the following:



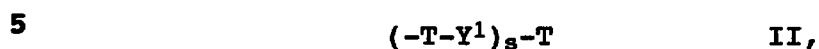
40 where

p and q are as defined above.

45 Y₁, Y₂ and Y₃ are preferably a direct bond, O, OCO, COO or OCOO.

5

The radicals M can in turn be the known mesogenic groups, in particular radicals containing aromatic or heteroaromatic groups. The mesogenic radicals conform, in particular, to the formula II



where the radicals

10 T, independently of one another, are cycloalkylene, heterocycloalkylene, aromatic or heteroaromatic radicals, the radicals

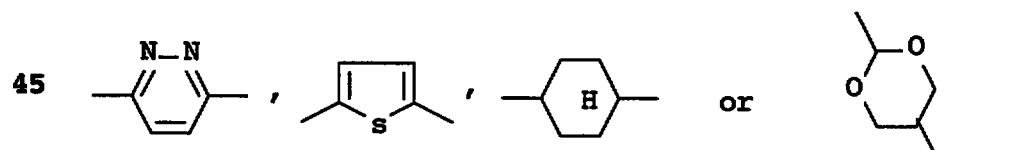
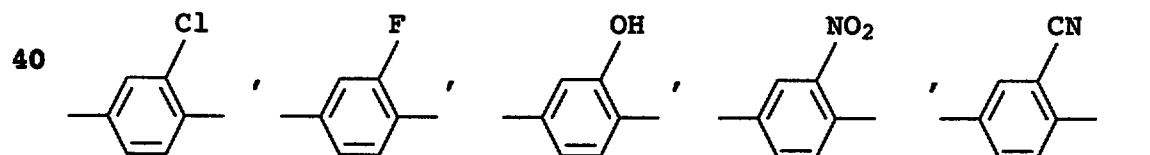
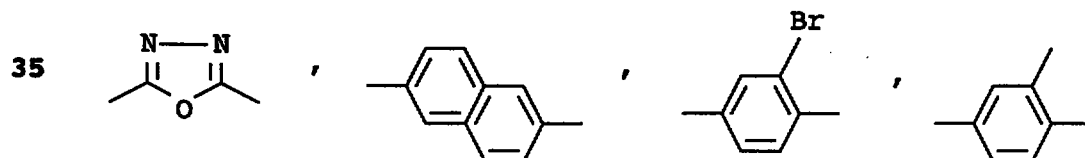
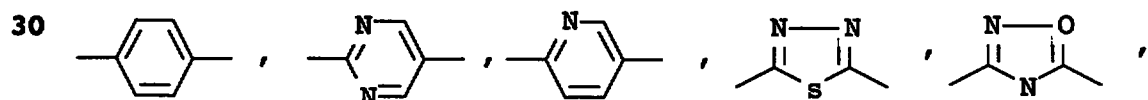
Y¹ independently of one another are O, COO, OCO, CH₂O, OCH₂, CH=N
15 or N=CH or a direct bond, and

s is from 1 to 3.

20 s is preferably 1 or 2.

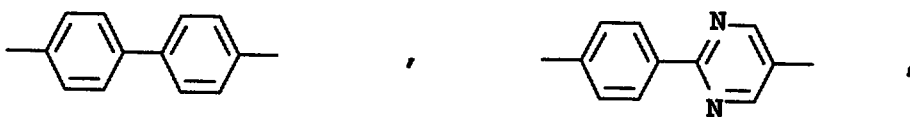
Y¹ is preferably -COO-, -OCO- or a direct bond.

The radicals T are generally carbocyclic or heterocyclic aromatic
25 ring systems, which may be substituted by fluorine, chlorine, bromine, cyano, hydroxyl or nitro, conforming, for example, to the following basic structures:

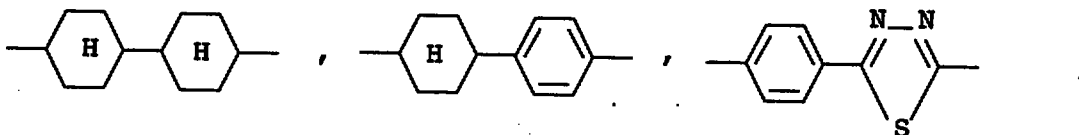


The mesogenic groups M are particularly preferably the following, for example:

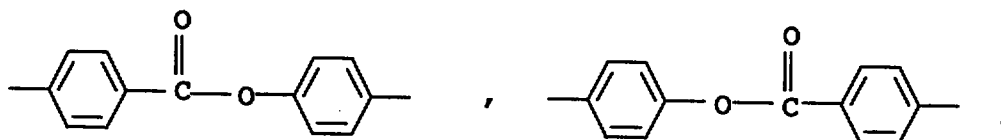
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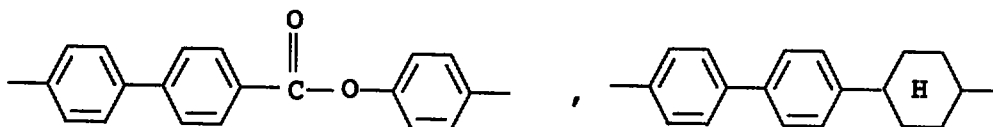
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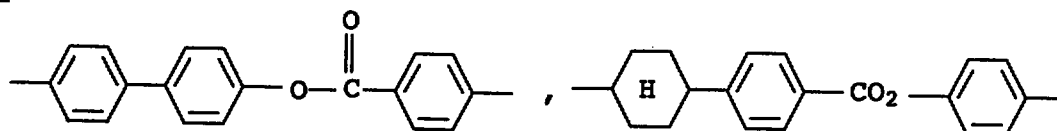


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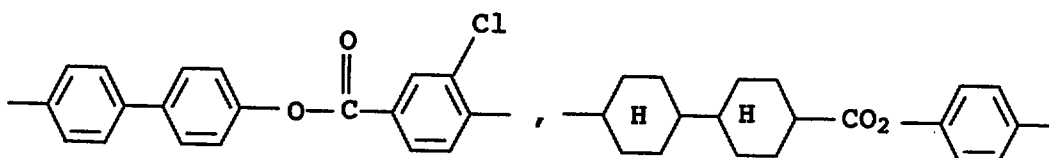


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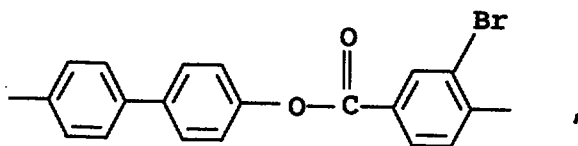
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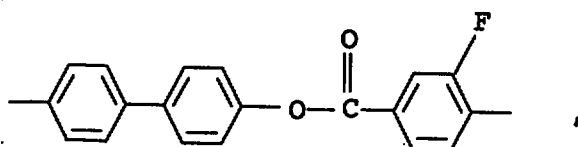
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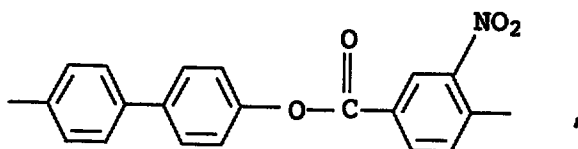
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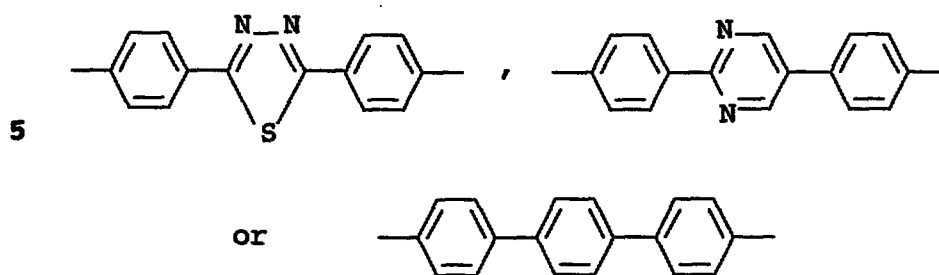


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- Preferred groups Z are those which can be polymerized by a photochemical initiation step, i.e. in particular groups of the structure : $\text{CH}_2=\text{CH}-$, $\text{CH}_2=\text{CCl}$, $\text{CH}_2=\text{C}(\text{CH}_3)-$ or 4-vinylphenyl.
- 15 Preference is given to $\text{CH}_2=\text{CH}-$, $\text{CH}_2=\text{CCl}-$ and $\text{CH}_2=\text{C}(\text{CH}_3)-$, particular preference being given to $\text{CH}_2=\text{CH}-$ and $\text{CH}_2=\text{C}(\text{CH}_3)-$.

- General methods for the preparation of the compounds of the formula I are known from the literature, for example the reaction with dicyclohexylcarbodiimide (DCC) for the preparation of esters. Details on the reactions are given in the examples, where parts and percentages are by weight, unless stated otherwise.
- 20

- 25 The compounds of the formula I are liquid-crystalline and can form smectic, nematic or cholesteric phases, depending on the structure. They are suitable for all purposes for which liquid-crystalline compounds are usually used.

- 30 Novel compounds adopt an intermediate position between low-molecular-weight and polymeric liquid-crystalline compounds. In contrast to polymers, they can be prepared reproducibly, have substantially uniform structures and nevertheless have viscosities similar to those of polymers.

35

- In order to establish desired properties, it may be expedient to use mixtures of compounds of the formula I or mixtures with other liquids, it being possible for these mixtures to be prepared in situ or by mechanical mixing.

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- The novel compounds are particularly suitable as alignment layers for liquid-crystalline materials, as photocrosslinkable adhesives, as monomers for the production of liquid-crystalline networks, as base material for the preparation of polymerizable liquid-crystal systems which can be doped by chiral compounds, as polymerizable matrix monomers for polymer-dispersed displays or as base material for polymerizable liquid-crystalline materials
- 45

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for optical components, such as polarizers, retardation plates or lenses. They are furthermore suitable in combination with low-molecular-weight, polymerizable liquid-crystalline compounds as film formers.

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The melting points in the examples were determined by means of a polarizing microscope. Temperature control was effected on a Mettler FP80/82 microscope heating stage.

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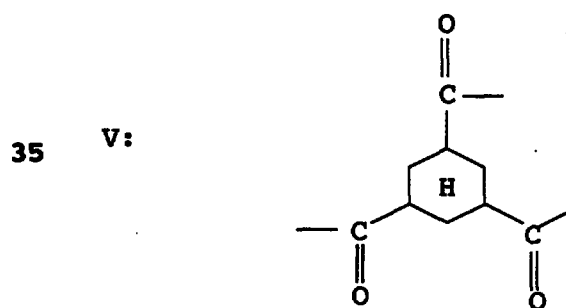
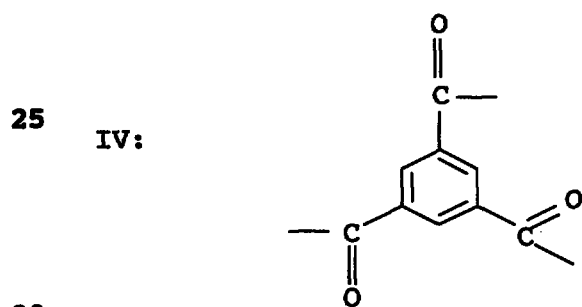
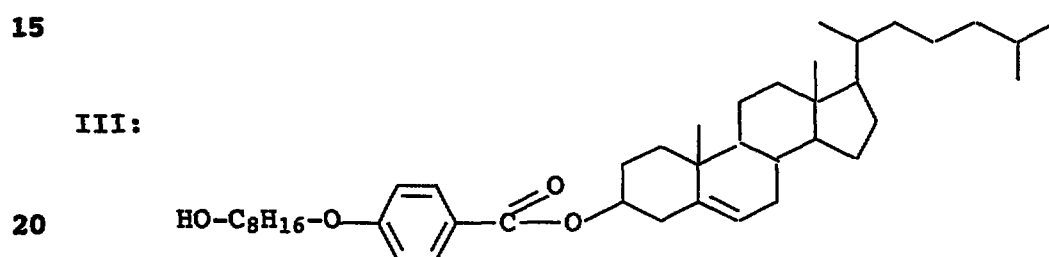
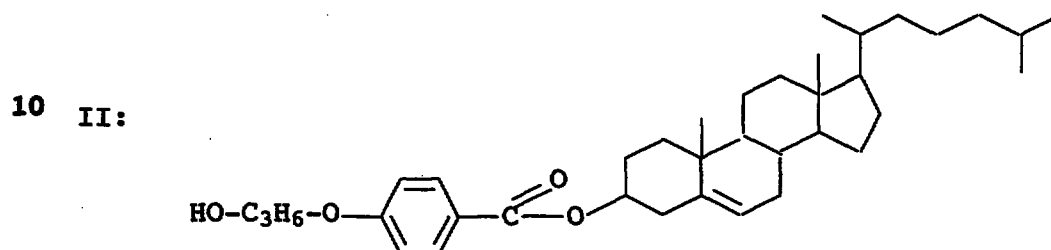
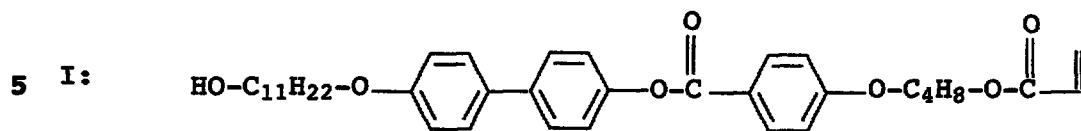
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Examples



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I, II and III are mesogens, and IV and V are central units.

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Example 1

1 ml of a solution of 13.6 g (0.05 mol) of 1,3,5-cyclohexanetricarbonyl chloride in 50 ml of absolute toluene is added at 60°C to a solution of 0.903 g (0.0015 mol) of I, 0.846 g (0.0015 mol) of II and 0.32 g of pyridine in 30 ml of toluene. The solution is stirred at 60°C for one hour and then at room temperature overnight. 50 ml of water are added, and the mixture is neutralized by means of 15 % strength hydrochloric acid. The organic phase is separated off, washed with water, dried using sodium sulfate and evaporated. Further purification is carried out by column chromatography (silica gel 60, toluene/ethyl acetate 3:1).

Yield: 1.45 g Phase behavior: n* polymerized

The compounds in the table below were prepared by methods similar to that in Example 1:

20

Ex.	Mesogen 1	Mesogen 2	Mixing ratio	Central unit	Phase behavior
2	I	II	1:1	IV	x 66 n* polymerized
3	I	III	1:1	V	n* polymerized
4	I	III	1:1	IV	n* polymerized
5	I	II	3:2	V	g s 96 n* 130 polymerized
6	I	II	3:2	IV	x 96 n* polymerized
7	I	III	3:2	V	x 68 n* polymerized
8	I	III	3:2	IV	x 38-42 n* polymerized

35

x = unidentified phase

g = glass state

s = smectic phase

n or n* = nematic or chiral nematic phase

i = isotropic phase

c = crystalline

The above compounds are all converted into polymers at elevated temperature.

Example 9

0.66 g (0.03 mol) of benzene-1,2,4,5-tetracarboxylic anhydride and 3.8 g of II are suspended in 15 ml of DMF, and the mixture is stirred at 110°C for 8 hours. The reaction product is precipitated by pouring into water, filtered off with suction, washed with water, dried at 50°C under reduced pressure and recrystallized from ethanol/toluene.

Yield: 2,7 g Solidification: 170-215°C.

1.49 g (0.001 mol) of the resultant reaction product, 1.2 g (0,002 mol) of I and 0.03 g (0.00022 mol) of pyrrolidinopyridine are dissolved in 40 ml of methylene chloride. 0.45 g (0.0022 mol) of dicyclohexylcarbodiimide are then added, and the mixture is stirred at room temperature overnight. The solution is filtered and evaporated, and the precipitated residue is chromatographed on silica gel 60 using toluene/glacial acetic acid 3:1.

Yield: 1 g Phase behavior: x 46-70 n* 160-180 i

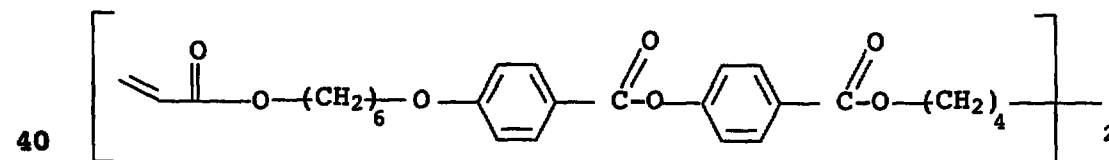
Example 10

The isomeric compounds are prepared by methods similar to that in Example 9, where benzene-1,2,4,5-tetracarboxylic anhydride is esterified first with III and then with I.

Yield: 500 mg Phase behavior: c 61-70 n* 168-186 i

Example 11

Preparation of



114 g (0.5 mol) of 4-benzyloxybenzoyl chloride are dissolved in a mixture of 150 ml of absolute CH₂Cl₂ and 9.6 g of pyridine. 7.3 g (0.55 mol) of 1,8-octandiol are then introduced at from 10 to 15°C, and the mixture is stirred overnight. The reaction product

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is precipitated by pouring into water and recrystallized from 250 ml of ethanol.

Yield: 25.1 g (= 88.7 % of theory)

5 Melting point: 90-91°C

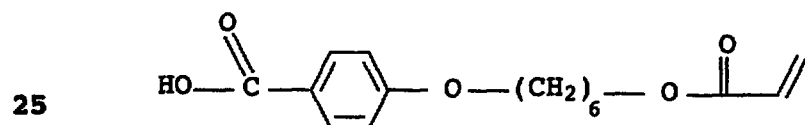
24.9 g (0.044 mol) of reaction product are dissolved in a mixture of 150 ml of toluene and 100 ml of ethanol, and 5.1 g of Raney nickel are added. The mixture is then hydrogenated for 1.5 hours at from 45 to 50°C with vigorous stirring. The H₂ consumption is 2.1 l under atmospheric pressure. The reaction product is separated off from the catalyst and filtered off. Further purification was unnecessary.

15

Yield: 16.8 g (= 98.9 % of theory)

Melting point: 182-183°C

0.97 g (0.0025 mol) of the resultant compound, 0.1 g of pyrrolidinopyridine and 1.53 g of compound of the formula



are dissolved in 50 ml of tetrahydrofuran. A solution of 1.5 g of dicyclohexylcarbodiimide in 5 ml of tetrahydrofuran is then added at from 5 to 10°C, and the mixture is stirred at 50°C for 4 hours and subsequently at room temperature overnight. The precipitated solid is filtered off, and the solution is evaporated. The residue is purified by column chromatography (silica gel 60, toluene/glacial acetic acid 3:1).

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Yield: 0.45 g

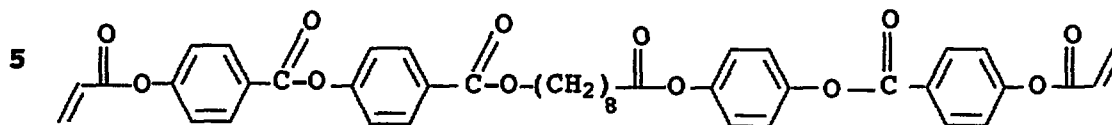
Phase behavior: c 77-82 n polymerized

The following compounds can be prepared analogously:

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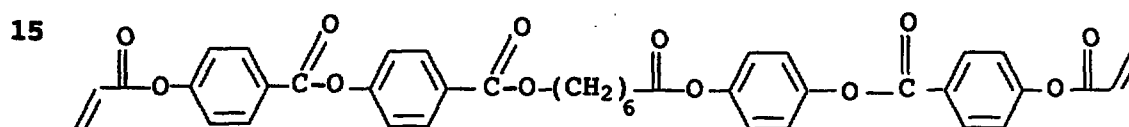
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Example 12



10 Phase behavior: c 116-144 n 154-156 i

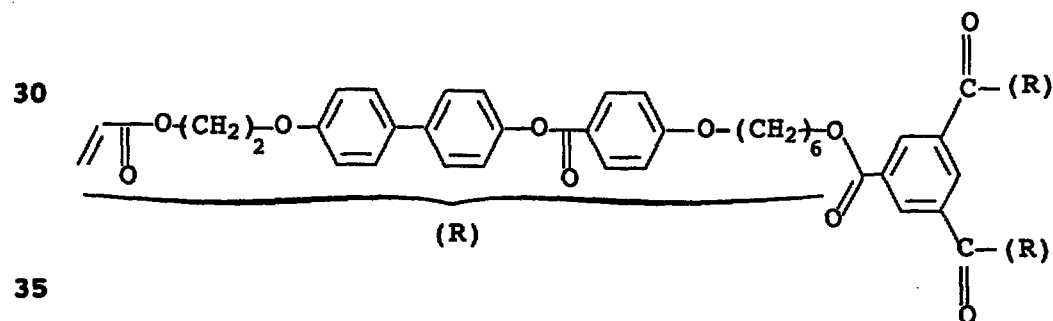
Example 13



20 Phase behavior: c 148 n 185 i

The following compounds can also be prepared analogously to Example 1:

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Example 14

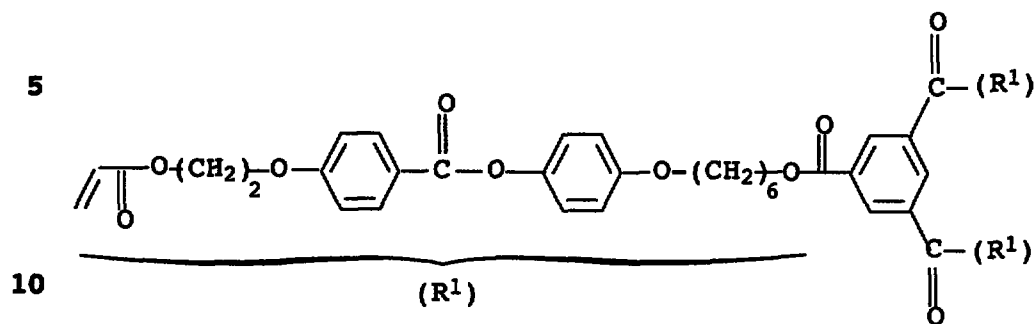


Phase behavior: c 86 n → polymerized

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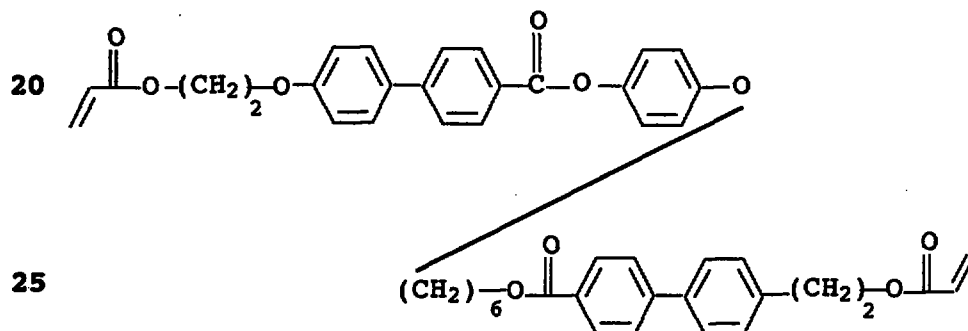
Example 15



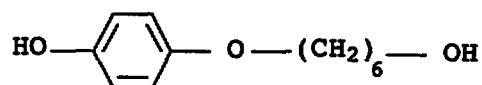
Phase behavior: c 100 n → polymerized

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Example 16



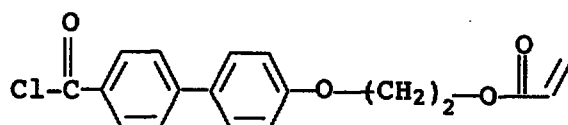
30 4.2 g (0.02 mol) of the compound of the formula



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are dissolved in 50 ml of tetrahydrofuran and 1.58 ml of pyridine. 6.77 g (0.04 mol) of the compound of the formula

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are added to this solution, and the mixture is stirred overnight. The reaction mixture is poured into HCl-acidified water, the solid is filtered off and taken up in methyl tert-butyl ether, and the resultant organic phase is washed by shaking repeatedly 5 with water. The solid obtained after evaporation is recrystallized from ethanol/toluene.

Yield: 3.45 g

Phase behavior: c 133 n → polymerized
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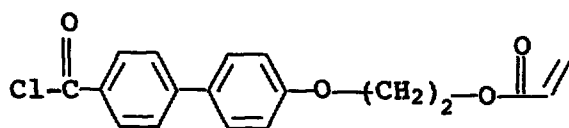
Example 17

60.4 g (0.4 mol) of methyl hydroxybenzoate and 2.6 g (0.02 mol) 15 of zinc(II) chloride are suspended in 180 ml of methylene chloride. After the mixture has been stirred at room temperature for 20 minutes, 16.2 (0.2 mol) of disulfur dichloride, dissolved in 20 ml of methylene chloride are added at room temperature over the course of 2 hours, and the mixture is then refluxed for 1 1/2 20 hours and stirred at room temperature for 48 hours. The reaction product is filtered off with suction, washed with methylene chloride, taken up in water and boiled for 1 hour. After cooling, the product is filtered off and dried.

Yield: 11.8 g Melting point: 170-172°C
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5.01 g (0.015 mol) of the resultant compound are dissolved in 50 ml of methylene chloride and 2.61 g (0.033 mol) of pyridine. 10.65 g (0.033 mol) of the compound of the formula

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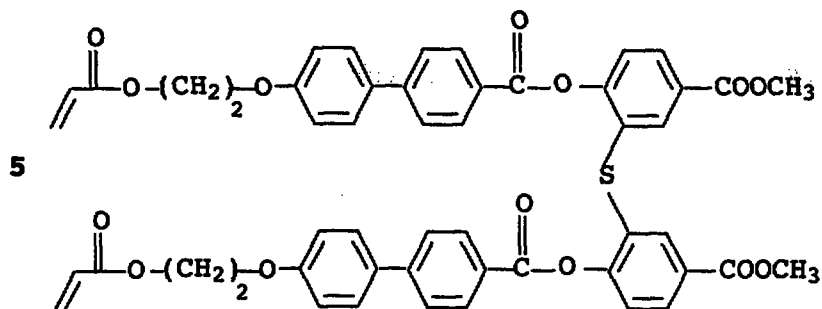
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dissolved in 20 ml of methylene chloride are added to this solution, and the mixture is then stirred at room temperature 40 overnight. For work-up, the reaction mixture is poured into water, and the precipitated solid is filtered off with suction and purified by chromatography (silica gel 60, toluene/THF 3:1)

Yield: 9.45 g c 159 → polymerized
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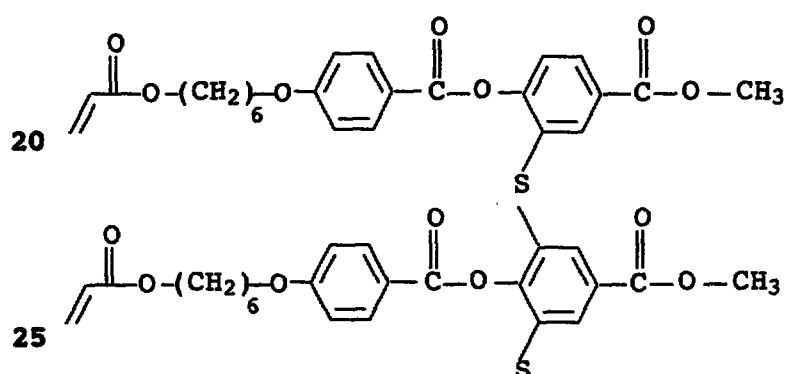
The compound conforms to the formula

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Example 18

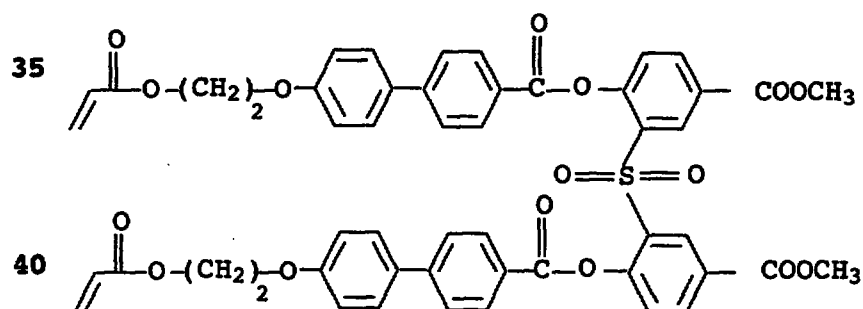
15 The compound of the formula



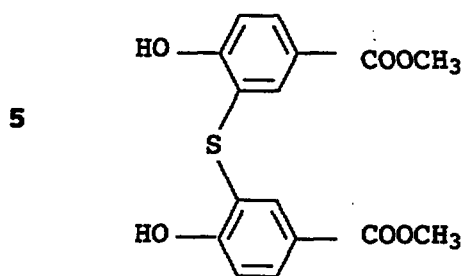
is also prepared analogously to Example 17. It polymerizes on heating.

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Example 19



45 4.34 g (0.015 mol) of the compound of the formula



are dissolved in 40 ml of glacial acetic acid, and 3.24 g (0.0286 mol) of perhydrol (30% strength in water) are added at room temperature.

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The mixture is then stirred at 100°C for 1 hour. After cooling, the product is precipitated by pouring into water, filtered off with suction, washed repeatedly with water and dried at 50°C under reduced pressure.

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Yield: 4.5 g

Melting point 210-221°C

Further reaction of the resultant compound analogously to Example 25 17 gives the above compound.

Yield: 2.75 g

30 c 199 polymerizes on transition into the liquid-crystalline phase.

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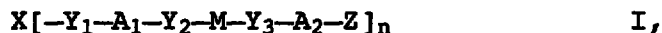
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We claim:

- 5 1. A compound of the formula I



where

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X is a silicon-free, n-valent central unit, the radicals

A₁ and A₂,

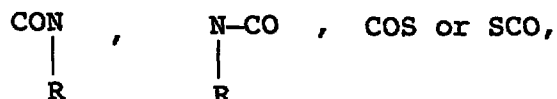
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independently of one another, are a direct bond or a spacer, the radicals

Y₁, Y₂ and Y₃,

20

independently of one another, are a direct bond, O, S, CO, OCO, COO, OCOO,



25

M is a mesogenic group,

Z is a polymerizable group, and

30

n is a number from 2 to 6, where

R is hydrogen, or C₁- to C₄-alkyl, and the combination of M-Y₃-A₂-Z can be a cholesteryl radical.

35

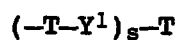
2. A compound as claimed in claim 1, where

X is an aliphatic, aromatic or cycloaliphatic radical or O, S, SO₂ or CO.

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3. A compound as claimed in claim 1, where M is a radical of the formula

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where the radicals

T, independently of one another, are aromatic or heteroaromatic radicals,

Y¹ independently of one another, are O, COO, OCO, CH₂O, OCH₂, CH=N or N=CH or a direct bond, and

s is from 1 to 3.

4. A compound as claimed in claim 1, where Z is a radical of the formula

CH₂=CH, CH₂=CCl or CH₂=C(CH₃)

5. The use of a compound as claimed in claim 1 as alignment layers for liquid-crystalline materials, as photocrosslinkable adhesives, as monomers for the production of liquid-crystalline networks, as base material for the preparation of polymerizable liquid-crystal systems which can be doped with chiral compounds, as polymerizable matrix monomers for polymer-dispersed displays or as base material for polymerizable liquid-crystalline materials for optical components, such as polarizers, retardation plates or lenses or in combination with low-molecular-weight, polymerizable liquid-crystalline compounds as film formers.