



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C09K 19/00, 19/38, C09B 67/00, C09D 5/36</p>	<p>A1</p>	<p>(11) International Publication Number: WO 98/42799</p> <p>(43) International Publication Date: 1 October 1998 (01.10.98)</p>
<p>(21) International Application Number: PCT/EP98/01453</p> <p>(22) International Filing Date: 13 March 1998 (13.03.98)</p> <p>(30) Priority Data: 97104854.1 21 March 1997 (21.03.97) EP (34) Countries for which the regional or international application was filed: DE et al.</p> <p>(71) Applicant (for all designated States except US): MERCK PATENT GMBH [DE/DE]; D-64271 Darmstadt (DE).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): POETSCH, Eike [DE/DE]; Am Buchwald 4, D-64367 Mühlthal 4 (DE). PFAFF, Gerhard [DE/DE]; Trautenauer Strasse 41, D-64839 Münster (DE). KUNTZ, Matthias [DE/DE]; Im Berggarten 16, D-64342 Seeheim (DE). DEROW, Stephan [DE/DE]; Stefan George Weg 11, D-64285 Darmstadt (DE). COATES, David [GB/GB]; 87 Sopwith Crescent, Merley Wimborne, Dorset BH21 1SW (GB).</p> <p>(74) Common Representative: MERCK PATENT GMBH; D-64271 Darmstadt (DE).</p>		<p>(81) Designated States: CN, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: PIGMENT FLAKES</p> <p>(57) Abstract</p> <p>The invention relates to pigment flakes comprising a chiral liquid crystalline polymer material, said chiral liquid crystalline polymer material serving as carrier material or being coated onto a carrier material, characterized in that the pigment flakes comprise at least one dye that is chemically bound to the polymer. The invention further relates to methods of manufacturing such pigment flakes and to the use of such pigment flakes in paints, printing inks, spray paints, cosmetic products or coloured plastics, optical elements and security applications.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Pigment Flakes

- 5 The invention relates to pigment flakes comprising a chiral liquid crystalline polymer material, said chiral liquid crystalline polymer material serving as carrier material or being coated onto a carrier material, characterized in that the pigment flakes comprise at least one dye that is chemically bound to the polymer.
- 10 The invention further relates to methods of manufacturing such pigment flakes and to the use of such pigment flakes in paints, printing inks, spray paints, cosmetic products or coloured plastics, optical elements and security applications.
- 15 Liquid crystals with chiral mesophases, in particular cholesteric liquid crystals, show extraordinary colour effects, like for example a high colour saturation, a wide colour range and iridescent appearance, due to their property of reflecting selected wavelengths of incident light. They have therefore been proposed for the preparation of pigments and inks.
- 20 In order to achieve good colour properties, a uniform and stable alignment of the liquid crystal molecules with the orientation of the helix axis parallel to the viewing direction is required. This can be achieved by preparing pigment flakes or platelets of a prealigned
- 25 cholesteric polymer material.
- Polymer pigment flakes are produced e.g. by coating a thin film of a cholesteric polymer material onto a substrate and aligning the material to achieve uniform orientation of the helical axis normal to
- 30 the surface of the substrate. The film is then cured and ground to yield small flat flakes. The pigment flakes can be dispersed e.g. in a transparent binder for the use as inks or paints. The pigment flakes and inks can be used at room temperature without the need of further
- 35 alignment.

Regarding the broad range of applications for chiral liquid crystal pigment flakes it is desirable for the expert to have available further pigments of this type which are easy to synthesize and fulfill the various requirements as described above.

5

Pigments comprising cholesteric liquid crystal polymers are described in prior art.

10

The European Patent 0 601 483 discloses cholesteric pigment flakes made of polysiloxanes with side chains comprising chiral cholesterol moieties and methacrylate groups as crosslinking agent.

15

However, the preparation of pigments according to the EP 0 601 483 is complicated as it requires at least three subsequent reaction steps wherein polymerizable material is used. First, a linear or cyclic polysiloxane backbone is prepared, onto which then side chains bearing chiral moieties and polymerizable methacrylate groups are attached. Finally the polymerizable side chains are crosslinked upon preparation of the pigment flakes.

20

Thus, there is a demand for chiral liquid crystal pigment flakes that can be made in a very simple manner which also enables easy and direct control of the optical and mechanical properties of the product.

25

Another important aspect of the present invention is to provide new materials for the preparation of liquid crystal pigment flakes. Thus, it has been found that, when the specific optical properties of a chiral liquid crystal polymer are combined with those of a fluorescent dye, which can be chemically linked to the liquid crystal polymer, it is possible to

30

achieve new pigments with extraordinary colour appearance.

The WO 95-32247 discloses interference pigments comprising liquid crystalline polymers which are made of mono- and difunctional nematic and chiral (meth)acrylates epoxides or vinyl ethers.

35

However, there is no hint to polymers comprising fluorescent dyes.

Liquid crystal polymers comprising dichroic or fluorescent dyes have been described in prior art for the use as optical storage materials or fluorescent displays, e.g. in the EP 090 282, EP 171 045, EP 260 687, EP 399 279, EP 422 535 or EP 630 954. However, these documents only mention linear polymers. They also give no hint to use the materials for the preparation of pigments.

One of the aims of the present invention is to provide pigment flakes which have the properties and advantages as described above, and which can be prepared in a simple way that also enables to easily and directly control the properties of the product.

Another aim of the invention is to extend the pool of liquid crystalline pigments available to the expert. Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.

The term 'flakes' as it is used throughout the claims and the description of this invention comprises small size particles with dimensions of 1 μm to 2 mm. These particles can be granules of a symmetric or unsymmetric shape as well as platelets having average lateral dimensions several times larger than the thickness, or mixtures of both platelets and granules. Platelet shaped pigment flakes are especially preferred.

The term 'chiral liquid crystalline polymer' as used throughout the claims and the description of this invention encompasses polymers that exhibit a chiral mesophase, like e.g. a chiral nematic (=cholesteric) or a chiral smectic phase. Polymers exhibiting a chiral nematic phase or a chiral smectic C phase are preferred. Particularly preferred are polymers exhibiting a chiral nematic phase.

The terms polymerizable or reactive mesogen, polymerizable or reactive mesogenic compound, polymerizable or reactive liquid crystal and polymerizable or reactive liquid crystalline compound as used in the foregoing and the following comprise compounds with a

5 rodlike, boardlike or disklike mesogenic group. These mesogenic compounds do not necessarily have to exhibit mesophase behaviour by themselves. In a preferred embodiment of the present invention they show mesophase behaviour in mixtures with other compounds or after polymerization of the pure mesogenic compounds or of the mixtures comprising the mesogenic compounds.

10 One of the objects of the present invention are pigment flakes comprising a chiral liquid crystalline polymer material, said chiral liquid crystalline polymer material serving as carrier material or being coated onto a carrier material, characterized in that the pigment flakes comprise at least one dye that is chemically bound to the liquid crystalline polymer.

15 Preferred embodiments of the present invention relate to

- Pigment flakes wherein at least one of the chemically bound dyes is a fluorescent dye.
- 20 • Pigment flakes that additionally comprise one or more dyes or pigments which are not chemically bound to the liquid crystalline polymer material.
- Pigment flakes wherein the liquid crystalline polymer material forms a three dimensional network.
- 25 • Pigment flakes with a thickness from 0.1 to 100 μm and lateral dimensions from 1 to 1000 μm .
- 30 • Pigment flakes wherein mica is used as carrier material.

Another object of the present invention are pigment flakes comprising a chiral liquid crystalline polymer material, said chiral liquid crystalline polymer material being coated onto a carrier material, wherein said pigment flakes are obtainable from a chiral

35

polymerizable mesogenic material by a process comprising the following steps

- 5 a) coating a thin layer of the chiral polymerizable mesogenic material onto the carrier material,
- b) aligning the chiral polymerizable mesogenic material in the coated layer into a uniform orientation,
- 10 c) polymerizing said chiral polymerizable mesogenic material by exposure to heat or actinic radiation.

Another object of the present invention are pigment flakes comprising a chiral liquid crystalline polymer material, said chiral liquid crystalline polymer material serving as carrier material, wherein said pigment flakes are obtainable from a chiral polymerizable mesogenic material by a process comprising the following steps

15

- 20 a) coating a thin layer of the chiral polymerizable mesogenic material onto a substrate or between two substrates,
- b) aligning the chiral polymerizable mesogenic material in the coated layer into a uniform orientation,
- 25 c) polymerizing said chiral polymerizable mesogenic material by exposure to heat or actinic radiation,
- d) optionally removing the substrate, or, if two substrates are present, one or both of the substrates from the polymerized material,
- 30 e) grinding the polymer film into small particles of the desired dimensions.

In a preferred embodiment of the present invention, the chiral polymerizable mesogenic material comprises at least two

35

polymerizable mesogenic compounds, at least one of which comprises a chromophoric group.

- 5 In another preferred embodiment of the present invention, the chiral polymerizable mesogenic material comprises at least one polymerizable mesogenic compound having one polymerizable functional group and at least one polymerizable mesogenic compound having two or more polymerizable functional groups.
- 10 In another preferred embodiment of the present invention the chiral polymerizable mesogenic material comprises at least one chiral polymerizable mesogenic compound and at least one achiral polymerizable mesogenic compound.
- 15 Another object of the present invention is the use of pigment flakes as effect pigments in paints, printing inks, spray paints, cosmetic products or coloured plastics, and for active and passive optical elements and security applications.
- 20 To induce the chiral phase behaviour in the polymerizable mesogenic material, for example a mixture comprising an achiral and a chiral mesogenic polymerizable compound can be used. For example, to induce cholesteric phase behaviour, a chiral nematic and an achiral nematic polymerizable compound are used. The chiral nematic
- 25 compound brings about the helically twisted cholesteric phase structure.
- Since the pitch of the cholesteric helix is depending on the chemical constitution and the concentration of the chiral compound, the wavelength of the reflection maximum and therewith the colour
- 30 properties of the flakes can be controlled directly in the production process just by varying the type and the ratio of the chiral mesogenic compound. Thus tailor-made pigment flakes with the desired colours can be prepared.
- 35 The ability of a chiral compound to induce a cholesteric structure structure with a certain helical pitch in a nematic host material is

called its helical twisting power (HTP). If a compound with a high HTP is used, only a small amount is sufficient to achieve a cholesteric structure with reflection of visible light. In this case it is not necessary that the chiral compound exhibits a liquid crystal phase per se. It is sufficient that the mixture of the chiral and achiral compounds shows a liquid crystal phase.

The pigment flakes according to the present invention either comprise a liquid crystalline polymer material which is coated onto a carrier material, or the liquid crystalline polymer material itself serves as the carrier material.

Pigment flakes comprising a carrier material are preferably prepared by the following method

- a) coating a thin layer of a chiral polymerizable mesogenic material onto the carrier material,
- b) aligning the chiral polymerizable mesogenic material in the coated layer into a uniform orientation,
- c) polymerizing said chiral polymerizable mesogenic material by exposure to heat or actinic radiation.

Preferably platelet shaped carrier materials are used. As carrier material for example natural or synthetic mica (muscovite or phlogopite), kaoline, talc, silica flakes, glass flakes or mixtures of two or more of these materials can be used.

In a preferred embodiment of the present invention mica is used as carrier material.

Pigment flakes wherein the liquid crystalline polymer material itself serves as the carrier material are preferably prepared by the following method

- a) coating a thin layer of a chiral polymerizable mesogenic material onto a substrate or between two substrates,
- 5 b) aligning the chiral polymerizable mesogenic material in the coated layer into a uniform orientation,
- c) polymerizing said chiral polymerizable mesogenic material by exposure to heat or actinic radiation,
- 10 d) optionally removing the substrate, or, if two substrates are present, one or both of the substrates from the polymerized material,
- e) grinding the polymer film into small particles of the desired dimensions.

15

The mixture of the achiral and chiral polymerizable mesogenic compounds is coated onto a substrate, aligned and cured into a polymer film. As a substrate for example a polyester (PET) film can be used. To achieve uniform alignment with planar orientation, i.e. 20 orientation of the helix axes normal to the surface of the coated mixture, the film can be sheared for example by means of a doctor's blade. In another preferred embodiment, a second PET layer is laminated on top of the coated material. In this case, the shearing caused by putting the two substrates together is sufficient to give 25 good alignment.

The alignment is preferably carried out in the cholesteric phase of the mixture of the mesogenic compounds prior to polymerization. Therefore alignment of a high quality can be achieved considerably 30 easier than for a coated polymer film as described in prior art due to the lower viscosity of the unpolymersed material. The application of electric or magnetic fields is not necessary.

35 Furthermore, since mixtures of polymerizable mesogenic monomers normally exhibit broad nematic or cholesteric mesophase ranges with relatively low melting temperatures, the polymerizable material can

be aligned and cured at low temperatures, preferably below 100 °C, in particular between 30 and 80 °C.

5 Due to the temperature dependency of the cholesteric pitch, the variation of the curing temperature leads to flakes with different maxima of selective reflection, thus providing another way to control the colour properties of the flakes, in addition to variation of the ratio of the chiral and achiral polymerizable mesogenic compounds.

10 Besides the above mentioned components, the mixture may comprise one or more other suitable components such as, for example, catalysts, light- or temperature-sensitive initiators, stabilizers, co-reacting monomers or surface-active compounds. It is
15 alternatively possible to add, for example, a quantity of up to 20% by weight of a nonpolymerizable liquid-crystalline material to adapt the optical properties of the product. It is also possible to add up to 10% of a non mesogenic compound with one or more polymerizable functional groups to increase crosslinking.

20 In some cases it is desirable to improve the wetting of the carrier material onto which the chiral polymerizable mesogenic material is coated. This can be of importance in particular when carrier materials with a polar surface, like e.g. mica, are used, which are then coated
25 with an inventive chiral polymerizable mesogenic material comprising unpolar mesogenic and chromophoric and/or fluorescent components.

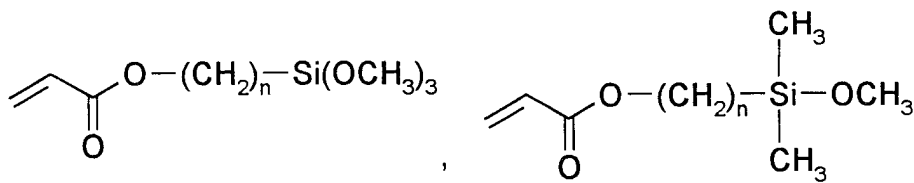
For the preparation of inventive pigment flakes comprising a carrier material that is covered by a chiral polymerizable mesogenic
30 material either by chemi- or physisorption, wherein the surface of the carrier material and the chiral polymerizable mesogenic material have different degree of polarity, the surface of the carrier material preferably is changed by wetting agents.

35 The use of wetting agents is particularly preferred for the preparation of inventive pigment flakes comprising a carrier material with a

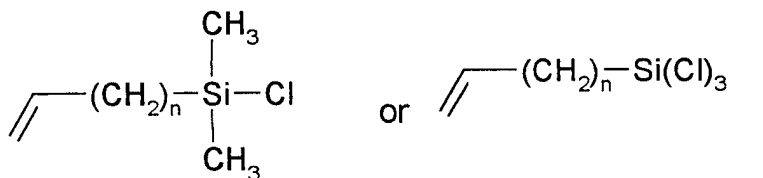
surface exhibiting high polarity and a chiral polymerizable mesogenic material exhibiting a moderate or weak polarity or being unpolar.

Wetting agents can be used which are either coreactive, like e.g.

5



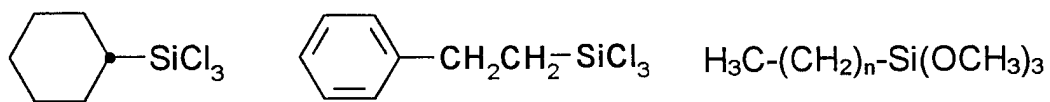
10



15

or which at least modify the surface by their unpolar headgroups, like e.g. the following compounds

20



or $(n\text{-C}_n\text{H}_{2n+1})_2\text{-SiCl}_2$, wherein n is from 1 to 9.

25

It is also possible to modify the surface of the carrier material by coreactive physisorbed wetting agents, e.g. by acrylates like for example pentaerythritol acrylate, which are coreactive with the other components that are coated on the surface of the carrier material.

30

Apart from the exemplary compounds specified above, it is also possible to use as wetting agents any other materials that are known to the skilled in the art for this purpose.

35

In the curing process the polymerizable groups of the aligned material react to form a crosslinked polymer film. Thereby the helical orientation is frozen in. The polymerization can be carried out for example by exposure to UV light with the help of a photoinitiator that decomposes under irradiation to produce free radicals that start the

polymerization reaction. In another preferred embodiment a cationic photoinitiator is used that photocures with cations instead of free radicals. The polymerization may also be started by an initiator that decomposes when heated above a certain temperature.

5

To exclude oxygen that may inhibit the free radical polymerization, a second PET layer may be laminated on top of the coated material, or alternatively the curing can be carried out under a nitrogen atmosphere. In the latter case shearing of the mesogenic material prior to polymerization is necessary to cause sufficient alignment of the cholesteric phase. When using a cationic photoinitiator oxygen exclusion is not needed, but water should be excluded.

10

15

These methods, however are only to be understood as examples that should not limit the scope of the invention. The person skilled in the art can easily find other suitable ways to carry out the polymerization.

20

Since the mixture may contain both polymerizable components with one (monofunctional) and with two or more polymerizable groups (multifunctional), polymerization and crosslinking are carried out in the same process.

25

By varying the concentration of the multifunctional mesogenic or non mesogenic components the crosslink density and thereby the product properties, such as the glass transition temperature, the temperature dependence of the optical properties, the thermal and mechanical stability and the solvent resistance can be tuned easily. According to the desired application e.g. films of a higher brittleness can be made by increasing the amount of multifunctional component. A higher brittleness is desirable in particular when the polymer film is subsequently ground to small flakes.

30

35

A high brittleness can also be achieved by using compounds with more than two polymerisable groups which may be mesogenic or non mesogenic. Typical examples for non mesogenic monomers with

more than two polymerisable groups are trimethylpropane-trimethacrylate or pentaerythritoltetraacrylate.

5 In addition to the dye groups which are chemically bound to the liquid crystalline polymer material, the pigment flakes additionally may comprise one or more dyes or pigments which are not chemically bound to the liquid crystalline polymer material. These dyes or pigments can be selected of conventional inorganic pigments (e.g. titanium dioxide, iron (III) oxide, iron oxide yellow, chromium oxide, iron blue, carbon black), organic pigments (e.g. azo-pigments, metal complex pigments, polycyclic pigments), or dyes (e.g. polymethine dyes or triphenylmethane dyes).

10

15 Flakes can be formed by grinding the cured polymer film, for example by means of a pestle and mortar or by using a mechanised grinder or mill. By additional cooling to temperatures below 0 °C the polymer brittleness is increased and grinding is made easier. The resulting powder is then sieved to give pigment flakes of the desired size.

20 A preferred method to produce flakes of spherical shape with dimensions smaller than 100 μm is grinding with a pestle and mortar by hand or in a mechanised mortar mill.

25 Another method to produce more or less spherical flakes is by milling the polymer film in a ball mill. Depending on the size and the weight of the balls, particles with average dimensions of less than 100 μm , in particular of 5 to 10 μm can be obtained.

30 Another preferred method is milling the polymer film under cooling in a blade mill. This produces a powder of platelet shaped flakes with lateral dimensions from several hundreds of microns to 1 to 2 mm. These flakes can subsequently be ground further in a mortar to give platelets with lateral dimensions smaller than 100 μm .

35 Cooling of the sample during grinding or milling can be achieved for example by using a carbon dioxide / acetone bath. Another preferred

method of cooling is the addition of dry ice powder or liquid nitrogen to the sample.

5 In some embodiments it is preferable to add an antistatic agent when milling the polymer material to avoid agglomeration of the particles.

Apart from the method described above, the following methods are preferred to produce chiral polymer flakes according to the invention:

- 10 • Coating the chiral polymerizable mesogenic material onto a substrate which contains shallow indentations with a diameter of 10 to 100 μm , preferably 20 to 50 μm and a depth of 3 to 20 μm , preferably 4 to 10 μm . In this case the act of coating causes
15 sufficient shear to give uniform alignment. In order to increase the quality of the alignment the material may additionally be sheared for example by means of a doctor's blade or by applying a second substrate on top of the coated material as described above.
- 20 • Gravure printing the chiral polymerizable mesogenic material in the shape of small droplets onto a substrate, for example a polyester web, using a gravure printing plate to leave droplets with a thickness of 3 to 20 μm , preferably 4 to 10 μm and a diameter of 10 to 100 μm , preferably 20 to 50 μm . The act of printing causes sufficient shear to give uniform alignment, however, here also the material may be
25 additionally aligned by shearing with for example a doctors blade or by applying a second substrate on top of the droplets.
- 30 • Spraying of the chiral polymerizable mesogenic material into an N_2 atmosphere to give small droplets with a diameter of 10 to 100 μm , which are cured by irradiation with strong UV light. The cured droplets may subsequently be ground to make smaller flakes.
- 35 • Coating the chiral polymerizable mesogenic material onto a rotating drum, aligning by a knife edge, curing by irradiation with UV light and scraping off the cured polymer to yield small flakes.

- Coating the chiral polymerizable mesogenic material onto a rotating drum containing dimples with a depth of 2 to 20 μm , preferably 3 to 10 μm and a diameter of 10 to 100 μm , preferably 20 to 50 μm , curing by UV irradiation and peeling off the drum.
5
- Coating the chiral polymerizable mesogenic material onto a rotating drum containing stripes that are 2 to 20 μm , preferably 3 to 10 μm deep and 10 to 100 μm , preferably 20 to 50 μm across, aligning and curing as described above. After this the stripes are ground into fragments of the desired size.
10
- Making an emulsion of the chiral polymerizable mesogenic material in an immiscible liquid and polymerising the droplets by heating or UV irradiation.
15
- Adding a surfactant to the chiral polymerizable mesogenic material and blowing N_2 gas in to make a foam which is polymerized, scraped off and ground.
20
- Extruding the chiral polymerizable mesogenic material under pressure through one or more slots with a width of 2 to 20 μm , preferably 3 to 10 μm , whereby the shearing produces good uniform alignment. The film is cured in an N_2 atmosphere.
25
- Another preferred method uses a solid particle, preferably carbon black or graphite dispersed in a solution of the chiral polymerizable mesogenic material and two solvents. Solvent 1 does not dissolve the chiral polymerizable mesogenic material but solvent 2 does. Solvent 2 is boiled off and the precipitating chiral polymerizable mesogenic material forms a coating over the carbon particle which is then polymerised. This method produces particularly bright flakes.
30

Further preferred methods and examples for the preparation of pigment flakes can be taken from the International Application WO
35

97/30136, the entire disclosure of which is incorporated into this application by way of reference.

5 The flakes obtained by the above mentioned methods have dimensions from 1 to 100 μm . It is also possible, however, to chose the process parameters so that flakes with dimensions larger than 100 μm , preferably from 0.5 mm to 1.5 mm, are obtained. These flakes show particularly striking colour effects and are preferred in certain applications.

10

Platelet shaped pigment flakes are preferred, wherein the aspect ratio, which describes the ratio of lateral dimensions to thickness, is larger than 3:1, in particular from 3:1 to 20:1, very preferably from 5:1 to 10:1.

15

Further preferred are pigments with a granular shape, wherein the aspect ratio is less than 10:1, particularly less than 3:1, especially preferably wherein thickness, length and width are approximately the same.

20

For the use in inks and paints, the cholesteric pigment flakes can be dispersed in a transparent binder or fluid, or incorporated into plastics, depending on the application.

25

For some applications, it is preferable to use mixtures of flakes with different reflection maxima.

30

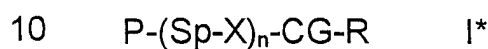
The cholesteric polymer flakes can be used as effect pigments in spraying or printing inks or paints or coloured plastics for decorative applications like for example cosmetic products. Other important fields of application are the automotive use, active or passive optical elements, like e.g. optical films such as polarizers or compensators, and security applications, for example in false-proof security labels such as ID cards, credit cards or tickets, or security marks e.g. for clothes which are visible in the dark.

35

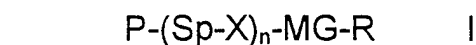
As explained in detail above, a considerable advantage of the invention resides in the fact that the optical and the mechanical

properties of the pigment flakes can all be controlled in the same process simply by changing the type and the concentration of the chiral and achiral, mono- and multifunctional, coloured and fluorescent mesogenic polymerizable compounds. Thus the pigment flakes can be tailored appropriately for the desired application.

The chiral polymerizable mesogenic material preferably comprises at least one polymerizable compound of formula I*



and optionally at least one polymerizable compound of formula I



wherein

P is a polymerizable group,

20 Sp is a spacer group having 1 to 20 C atoms,

X is a group selected from -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -O-SO₂-, -SO₂-O- or a single bond,

25 n is 0 or 1,

R is H or an alkyl radical with up to 25 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -O-SO₂-, -SO₂-O- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, or alternatively R is halogen, cyano or has independently one of the meanings given for P-(Sp-X)_n,

35 MG is a mesogenic or mesogeneity supporting group,

CG is a chromophoric or fluorescent chromophoric group which can in addition be chiral and/or mesogenic.

5 In a preferred embodiment of the invention the polymerizable mesogenic compounds are selected according to formula I and/or I*, wherein R has one of the meanings of P-(Sp-X)_n- as given above.

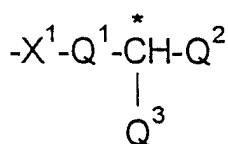
10 P in formula I and I* is preferably selected from CH₂=CW-COO-,
 WCH=CH-O-, $\text{WHC} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{---} \end{array} \text{CH-}$ or CH₂=CH-Phenyl-(O)_k- with W being H, CH₃ or Cl and k being 0 or 1,

15 P is particularly preferably a vinyl group, an acrylate group, a methacrylate group, a propenyl ether group or an epoxy group, very particularly preferably an acrylate or methacrylate group.

20 If R in the compounds of formula I and I* is an alkyl or alkoxy radical, i.e. where the terminal CH₂ group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, nonoxy,
 25 decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

30 Oxaalkyl, i.e. where one CH₂ group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

35 In the polymerizable mesogenic compounds of formula I and I* R may be an achiral or a chiral group. In case of a chiral group it is preferably selected according to the following formula IV:



IV

5

wherein

X^1 has the meaning given for X,

10

Q^1 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond,

15

Q^2 is an alkyl or alkoxy group with 1 to 10 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by - $\text{C}\equiv\text{C}$ -, -O-, -S-, -NH-, -N(CH_3)-, -CO-, -COO-, -OCO-, -OCO-O-, -SO₂-O- or -O-SO₂- in such a manner that oxygen atoms are not linked directly to one another, or alternatively has the meaning given for P-Sp-,

20

Q^3 is halogen, a cyano group or an alkyl or alkoxy group with 1 to 4 C atoms different from Q^2 .

25

Preferred chiral groups R are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chlorpropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy,

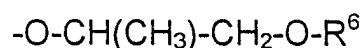
35

1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, for example.

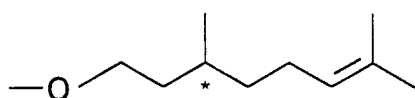
5 In addition, mesogenic compounds of the formula I and I* containing an achiral branched group R can be of importance as comonomers, for example, as they reduce the tendency towards crystallization. Branched groups of this type generally do not contain more than one chain branch. Preferred branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-
10 methylpropoxy and 3-methylbutoxy.

In another preferred embodiment R in formula I or I* is denoting a chiral group that is selected from the following groups:

15 an ethylenglycol derivative



20 wherein R⁶ is an alkyl radical with 1 to 12 C atoms, or a group based on citronellol.



25 As for the spacer group Sp in formula I and I* all groups can be used that are known for this purpose to the skilled in the art. The spacer group Sp is preferably linked to the polymerizable group P by an ester or ether group or a single bond. The spacer group Sp is preferably a
30 linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more non-adjacent CH₂ groups may be replaced by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -O-CO-, -CO-O-, -O-CO-O-, -SO₂-O-, -O-SO₂-, -CH(halogen)-, -CH(CN)-, -CH=CH- or -C≡C-.

35

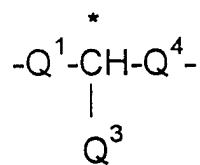
Typical spacer groups Sp are for example $-(\text{CH}_2)_o-$, $-(\text{CH}_2\text{CH}_2\text{O})_r-$, CH_2CH_2- , $-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2-$, with o being an integer from 2 to 12 and r being an integer from 1 to 3.

5 Preferred spacer groups Sp are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene and 1-methylalkylene, for example.

10

In a preferred embodiment of the invention the polymerizable mesogenic compounds of formula I and I* comprise a spacer group Sp that is a chiral group of the formula V:

15



V

20

wherein

Q^1 and Q^3 have the meanings given in formula IV, and

25

Q^4 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q^1 .

In the event that R or Q^2 are a group of formula P-Sp-X- or P-Sp- respectively, the spacer groups on each side of the mesogenic core may be identical or different.

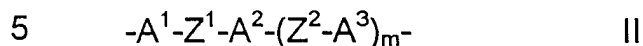
30

In particular preferred are compounds of formula I and I* wherein n is 1.

35

In a preferred embodiment, the inventive anisotropic polymers and cholesteric polymer films are obtainable by copolymerizing mixtures comprising compounds of formula I and/or I* wherein n is 0 and compounds of formula I and/or I* wherein n is 1.

The mesogenic group MG in formula I is preferably selected of formula II:



with

10 A^1 , A^2 and A^3 being independently from one another 1,4-phenylene in which, in addition, one or more CH groups may be replaced by N, 1,4-cyclohexylene in which, in addition, one or two non-adjacent CH_2 groups may be replaced by O and/or S, 1,4-cyclohexenylene or naphthalene-2,6-diyl, it being possible for all these groups to be unsubstituted,
 15 mono- or polysubstituted with halogen, cyano or nitro groups or alkyl, alkoxy or alkanoyl groups having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl,

20 Z^1 and Z^2 being independently from one another -O-, -CO-, -COO-, -OCO-, -O-SO₂-, -SO₂-O-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond and

25 m being 0, 1 or 2,

Bicyclic and tricyclic mesogenic compounds are preferred.

30 Of the compounds of formula I especially preferred are those in which R is F, Cl, cyano, or optionally halogenated alkyl or alkoxy, or has the meaning given for P-(Sp-X)_n-, and MG is of formula II wherein Z^1 and Z^2 are -COO-, -OCO-, -CH₂-CH₂-, -CH=CH-COO-, -OCO-CH=CH- or a single bond.

35 A smaller group of preferred mesogenic groups MG of formula II is listed below. For reasons of simplicity, Phe in these groups is 1,4-

phenylene, Phe L is a 1,4-phenylene group which is substituted by at least one group L, with L being F, Cl, CN, NO₂ or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 4 C atoms, and Cyc is 1,4-cyclohexylene.

5	-Phe-Z ¹ -Phe-	II-1
	-Phe-Z ¹ -Cyc-	II-2
	-PheL-Z ¹ -Phe-	II-3
	-PheL-Z ¹ -Cyc-	II-4
10	-Phe-Z ¹ -PheL-	II-5
	-Phe-Z ¹ -Phe-Z ² -Phe-	II-6
	-Phe-Z ¹ -Phe-Z ² -Cyc-	II-7
	-Phe-Z ¹ -Phe-Z ² -PheL-	II-8
	-Phe-Z ¹ -PheL-Z ² -PheL-	II-9
15	-Phe-Z ¹ -Cyc-Z ² -Phe-	II-10
	-Phe-Z ¹ -Cyc-Z ² -Cyc-	II-11
	-Phe-Z ¹ -PheL-Z ² -Phe-	II-12
	-Phe-Z ¹ -Phe-Z ² -PheL-	II-13
	-PheL-Z ¹ -Phe-Z ² -PheL-	II-14
20	-PheL-Z ¹ -PheL-Z ² -Phe-	II-15
	-PheL-Z ¹ -PheL-Z ² -PheL-	II-16

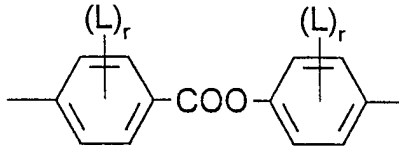
In these preferred groups Z¹ and Z² have the meaning given in formula I described above. Preferably Z¹ and Z² are -O-, -COO-,
 25 -OCO-, -CO-, -O-SO₂-, -SO₂-O-, -CH₂CH₂- or a single bond.

PheL in this preferred formulae is very preferably denoting 1,4-phenylene which is monosubstituted with L in the 2- or 3-position or disubstituted with L in the 2- and 3-position or in the 3- and 5-
 30 position, with L having each independently one of the meanings given above.

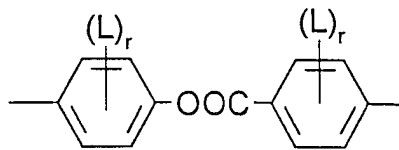
L is preferably F, Cl, CN, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, CF₃, OCF₃, OCHF₂, OC₂F₅, in particular F, Cl, CN, CH₃,
 35 C₂H₅, OCH₃, COCH₃ and OCF₃, most preferably F, CH₃, OCH₃ and COCH₃.

MG in formula I particularly preferably has one of the following meanings

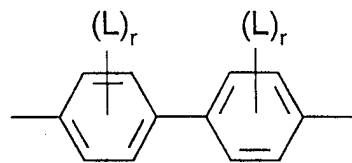
5



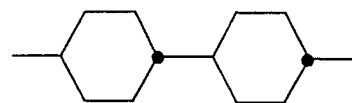
10



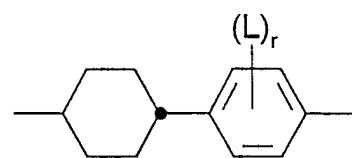
15



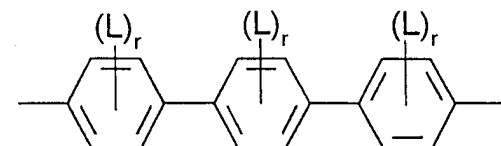
20



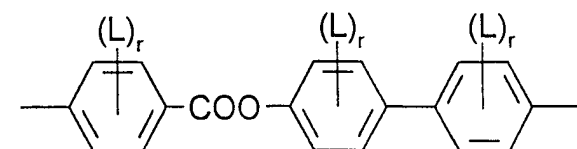
25



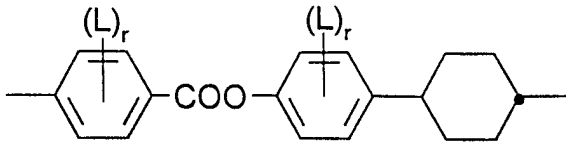
30



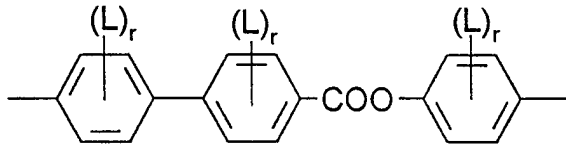
35



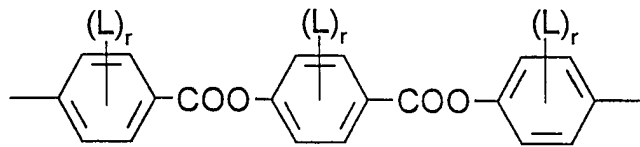
5



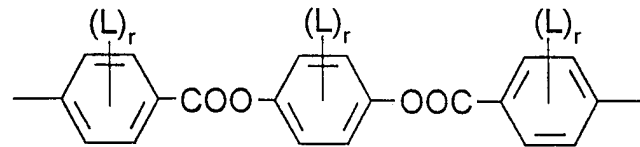
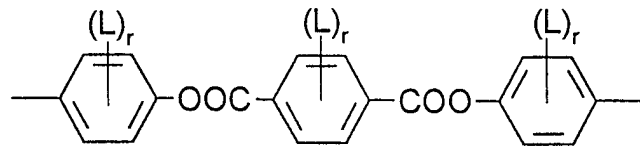
10



15

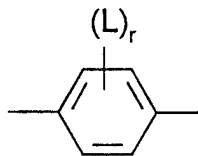


20



wherein L has the meaning given above and r is 0, 1 or 2.

25

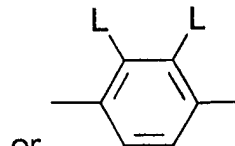
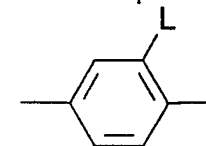
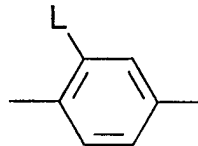


The group

in this preferred formulae is very preferably

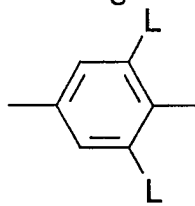
30

denoting



, furthermore

35

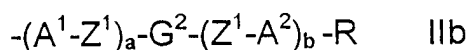
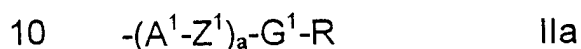


, with L having each independently one of the meanings given above.

- 25 -

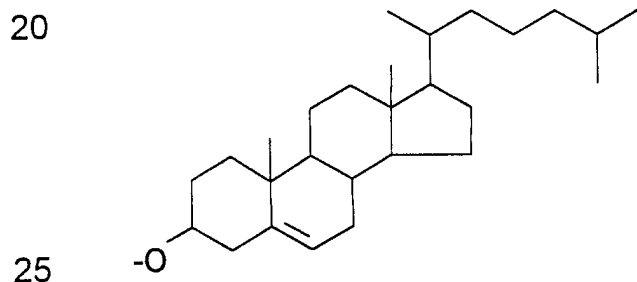
R in these preferred compounds is particularly preferably CN, F, Cl, OCF_3 , or an alkyl or alkoxy group with 1 to 12 C atoms or has one of the meanings given for $\text{P}-(\text{Sp-X})_n$.

5 In another preferred embodiment of the present invention the compounds of formula I are chiral compounds which comprise a group MG having at least one center of chirality. In these compounds MG-R is preferably selected according to formula IIa or IIb:

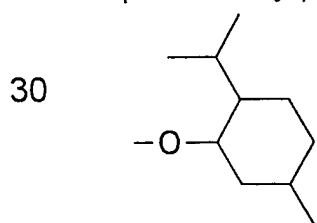


15 wherein A^1 , A^2 and Z^1 have the meaning given in formula II, R has one of the meanings given in formula I, with R in formula IIa denoting H, a and b are independently of each other 0, 1 or 2,

$-\text{G}^1\text{-R}$ in formula IIa is a terminal chiral group, such as for example a cholesteryl group,



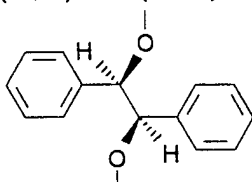
a terpenoid radical, like e.g. disclosed in the WO 96/17901, particularly preferably a menthyl group,



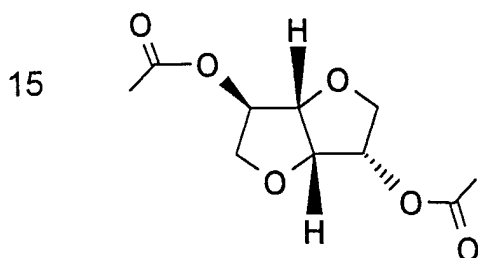
35 or a terminal chiral sugar derivative comprising a mono- or dicyclic radical with pyranose or furanose rings like, for example, a terminal

group derived from the chiral sugars or sugar derivatives as disclosed e.g. in the international application WO 95/16007,

5 and G^2 in formula IIb is a bivalent chiral group, like for example a (S,S)- or (R,R)-hydrobenzoin group



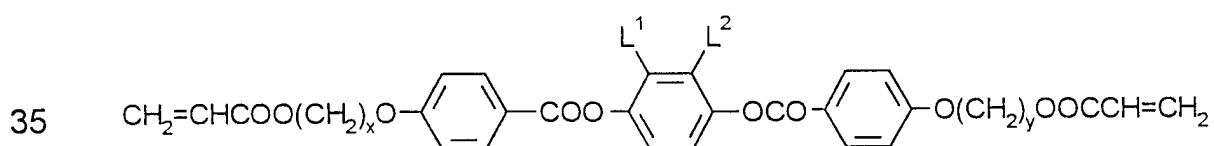
10 or a bivalent chiral sugar, sugar derivative or another bivalent chiral radical, as disclosed e.g. in the international application WO 95/16007, especially preferably a group based on 1,4:3,6-Dianhydro-D-sorbitol:

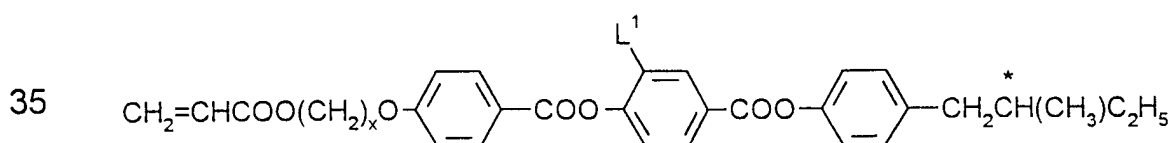
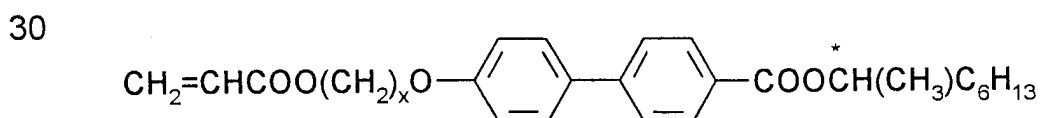
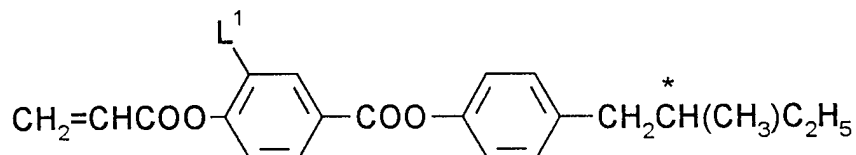
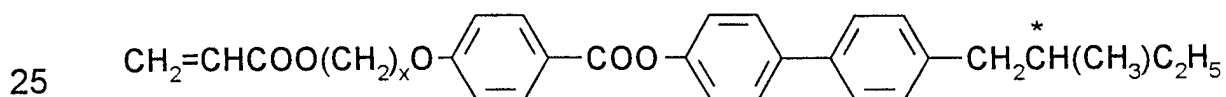
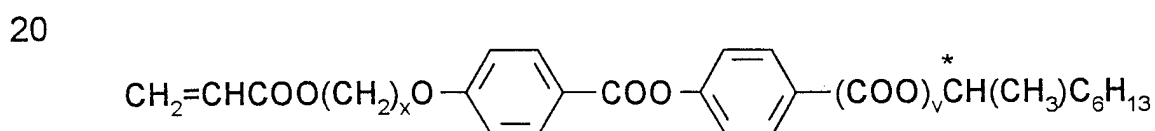
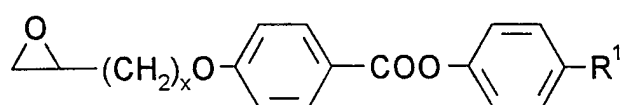
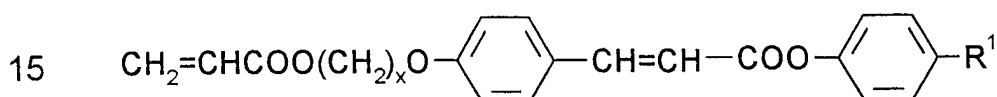
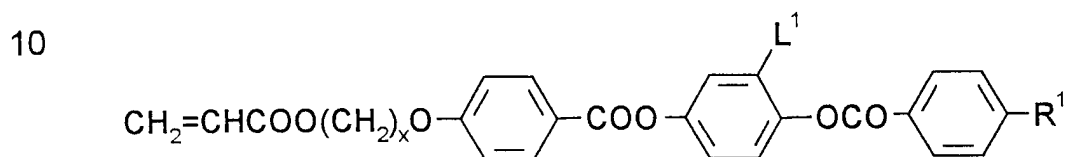
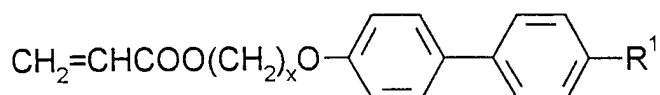
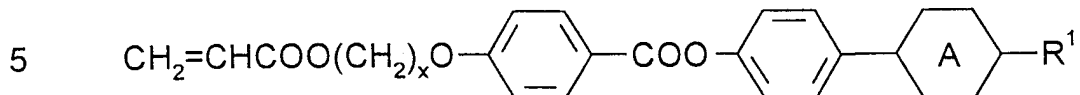
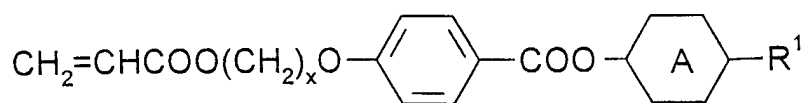


20 In case G^2 is a group based on 1,4:3,6-Dianhydro-D-sorbitol as disclosed above, Z is preferably denoting $-\text{CH}=\text{CH}-$.

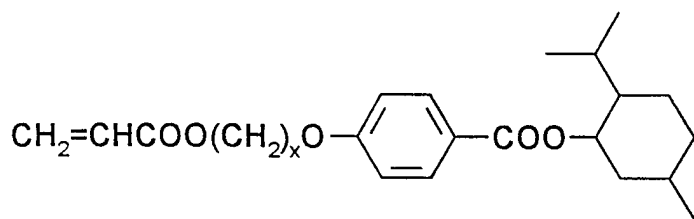
25 Typical examples representing polymerizable mesogenic compounds of the formula I can be found in WO 93/22397; EP 0 261 712; DE 195 04 224; DE 44 08 171 or DE 44 05 316. The compounds disclosed in these documents, however are to be regarded merely as examples that should not limit the scope of this invention.

30 Furthermore, typical examples representing polymerizable mesogenic compounds like those of formula I are shown in the following list of compounds, which is, however, to be understood only as illustrative without limiting the scope of the present invention:

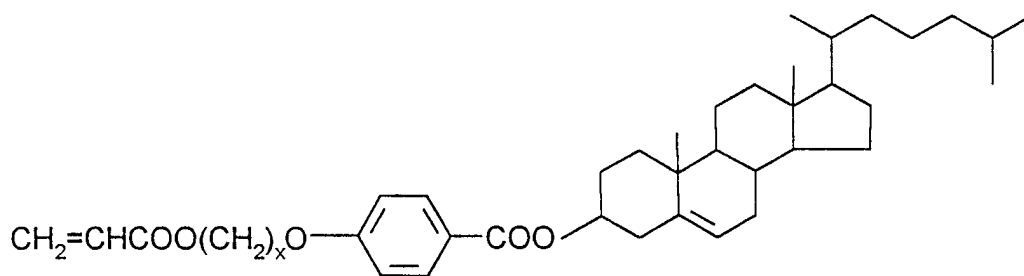




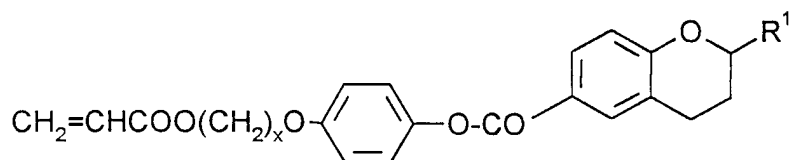
5



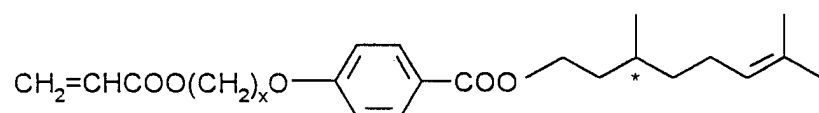
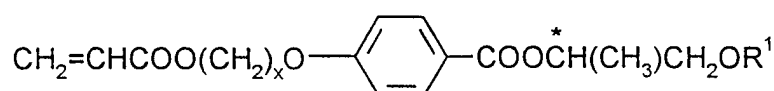
10



15



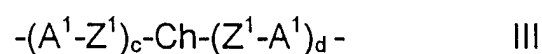
20



In these compounds x and y are each independently 1 to 12, A is a 1,4-phenylene or 1,4-cyclohexylene group, R¹ is halogen, cyano or an optionally halogenated alkyl or alkoxy group with 1 to 12 C atoms and L¹ and L² are each independently H, F, Cl, CN, or an optionally halogenated alkyl, alkoxy or alkanoyl group with 1 to 7 C atoms.

30

The chromophoric group CG in formula I* is preferably selected of the following formula



35

wherein

A¹ and Z¹ each independently have the meaning given in formula II,

5 c and d are 0, 1 or 2,

Ch is a chromophore or a fluorescent chromophore, which can in addition be chiral and/or mesogenic.

10

Of the compounds of formula I* especially preferred are those in which R is H, alkyl or alkoxy or has the meaning given for P-(Sp-X)_n-, X is -O-, -CO-, -COO-, -OCO-, -SO₂-O-, -O-SO₂- or a single bond, and CG is of formula III, wherein Z¹ is -O-, -COO-, -OCO-, -CO-, -SO₂-O-, -O-SO₂- or a single bond.

15

A smaller group of preferred chromophoric groups CG of formula III is listed below. In these groups, Phe, Phe L and Cyc have the meaning given in formulae II-1 to II-16 above. The following list comprises the preferred formulae III-1 to III-32 as well as their corresponding mirror images.

20

	-Ch-Z ¹ -Phe-	III-1
	-Ch-Z ¹ -Cyc-	III-2
25	-Ch-Z ¹ -PheL-	III-3
	-Ch-Z ¹ -Phe-Z ¹ -Phe-	III-4
	-Ch-Z ¹ -Phe-Z ¹ -PheL-	III-5
	-Ch-Z ¹ -Phe-Z ¹ -Cyc-	III-6
30	-Ch-Z ¹ -PheL-Z ¹ -PheL-	III-7
	-Ch-Z ¹ -PheL-Z ¹ -Cyc-	III-8
	-Ch-Z ¹ -Cyc-Z ¹ -Cyc-	III-9
	-Ch-Z ¹ -Cyc-Z ¹ -Phe-	III-10
	-Ch-Z ¹ -Cyc-Z ¹ -PheL-	III-11

35

	-Phe-Z ¹ -Ch-Z ¹ -Phe-	III-12
	-Phe-Z ¹ -Ch-Z ¹ -Cyc-	III-13
	-Phe-Z ¹ -Ch-Z ¹ -PheL-	III-14
	-PheL-Z ¹ -Ch-Z ¹ -PheL-	III-15
5	-Cyc-Z ¹ -Ch-Z ¹ -Phe-	III-16
	-Cyc-Z ¹ -Ch-Z ¹ -Cyc-	III-17
	-Cyc-Z ¹ -Ch-Z ¹ -PheL-	III-18
	-Phe-Z ¹ -Phe-Z ¹ -Ch-Z ¹ -PheL-	III-19
10	-Phe-Z ¹ -PheL-Z ¹ -Ch-Z ¹ -PheL-	III-20
	-PheL-Z ¹ -PheL-Z ¹ -Ch-Z ¹ -PheL-	III-21
	-Phe-Z ¹ -Cyc-Z ¹ -Ch-Z ¹ -PheL-	III-22
	-Cyc-Z ¹ -Cyc-Z ¹ -Ch-Z ¹ -PheL-	III-23
15	-Phe-Z ¹ -Ch-Z ¹ -Phe-Z ¹ -Phe-	III-24
	-Phe-Z ¹ -Ch-Z ¹ -Phe-Z ¹ -Cyc-	III-25
	-Phe-Z ¹ -Ch-Z ¹ -Phe-Z ¹ -PheL-	III-26
	-Phe-Z ¹ -Ch-Z ¹ -PheL-Z ¹ -PheL-	III-27
20	-Phe-Z ¹ -Phe-Z ¹ -Ch-Z ¹ -Phe-Z ¹ -Phe-	III-28
	-Phe-Z ¹ -PheL-Z ¹ -Ch-Z ¹ -Phe-Z ¹ -PheL-	III-29
	-Cyc-Z ¹ -Cyc-Z ¹ -Ch-Z ¹ -Cyc-Z ¹ -Cyc-	III-30
	-Phe-Z ¹ -PheL-Z ¹ -Ch-Z ¹ -Cyc-Z ¹ -Cyc-	III-31
	-Phe-Z ¹ -PheL-Z ¹ -Ch-Z ¹ -Phe-Z ¹ -Cyc-	III-32

25

In these preferred formulae, Z¹, PheL and L have the preferred meanings as described for the formulae II-1 to II-16 above. R in the preferred compounds has the preferred meanings as given above.

30

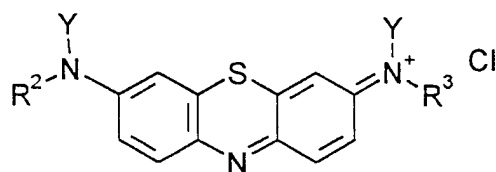
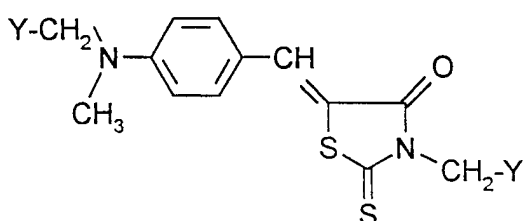
35

As chromophoric group Ch in principle every chromophoric group may be used that is known to the skilled in the art. Following is a list of typical examples for chromophoric groups Ch of the formula III. This list is, however, only to be understood as explaining, but not limiting the scope of the present invention.

5

Y in these formulae is denoting a single bond.

10

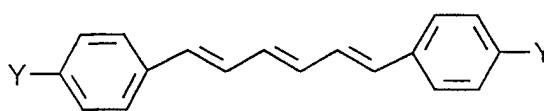
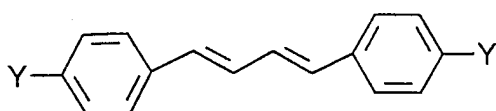


15

5-(p-dimethylaminobenzylidene)-
rhodanine

thionine derivatives, wherein R²,
R³ and R⁴ are H or C₁₋₁₂ alkyl,

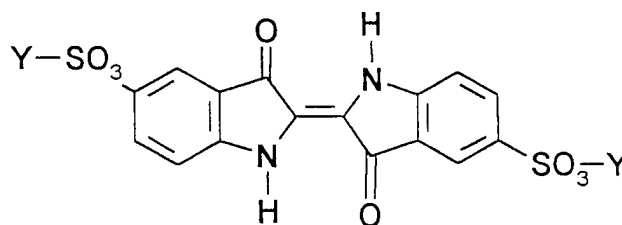
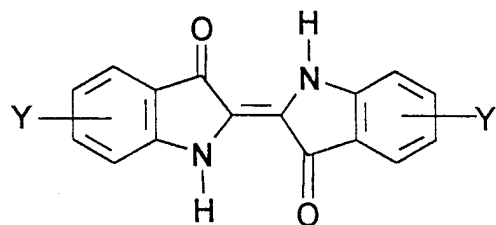
20



1,4-diphenyl-1,3-butadiene (DPB),

1,6-diphenyl-1,3,5-hexatriene(DPH),

25



30

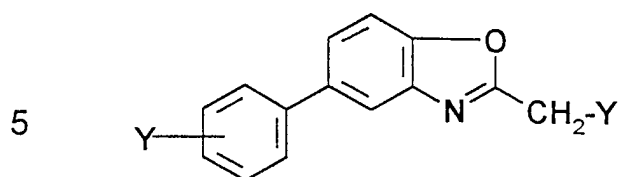
indigotine or

indigocarmine

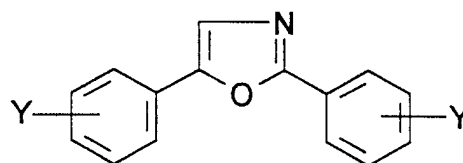
and their substitution products,

35

oxazole derivatives, like e.g.

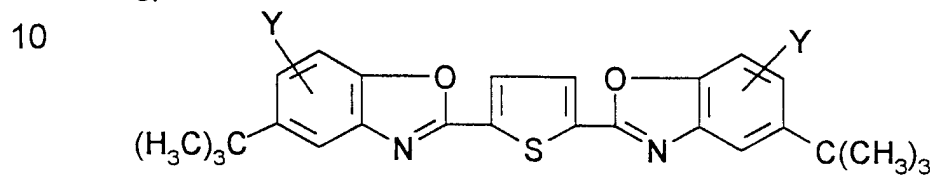


2-methyl-5-phenylbenzoxazole



2,5-diphenyloxazole (PPO)

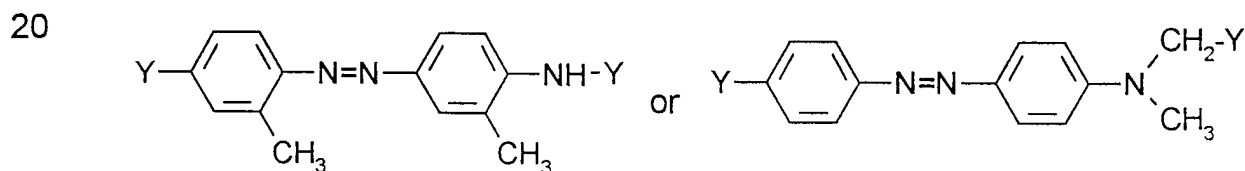
or



2,5-bis-(5'-tert.-butyl-2-benzoxazolyl)thiophene (BBOT),

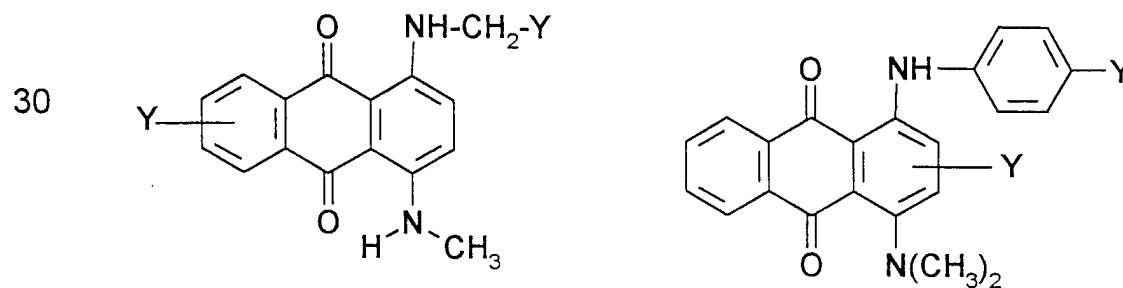
15

azo dyes, such as



25

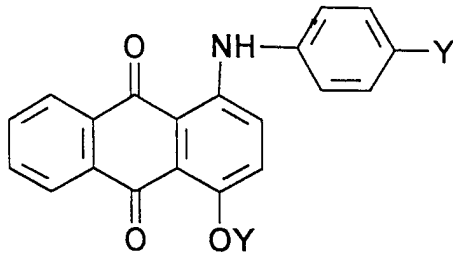
or anthraquinone derivatives, such as



35

or

5



10

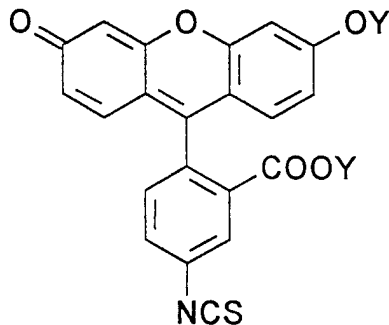
Particularly preferred are compounds of formula I* wherein CG is representing a fluorescent chromophoric group. When using a chiral polymerizable mesogenic material comprising compounds of formula I* that are bearing such a fluorescent chromophoric group, pigment flakes can be obtained that show particularly striking colour effects.

15

Typical examples for fluorescent chromophoric groups Ch in formula III can be taken from the following list, which should only illustrate the scope of the present invention without limiting it.

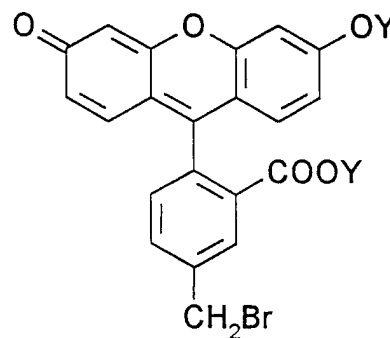
Fluorescein derivatives, like e.g.

20



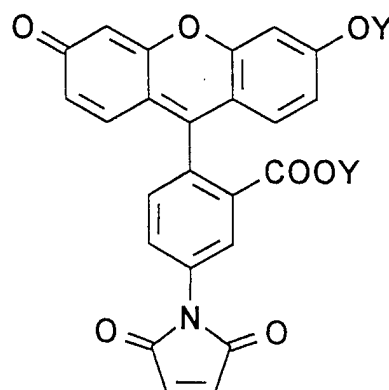
25

fluorescein-5-isothiocyanate
or



5-(bromomethyl)fluorescein

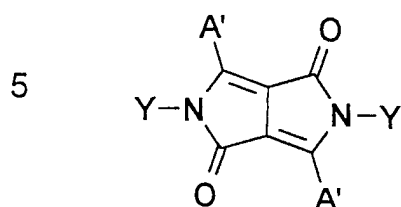
30



35

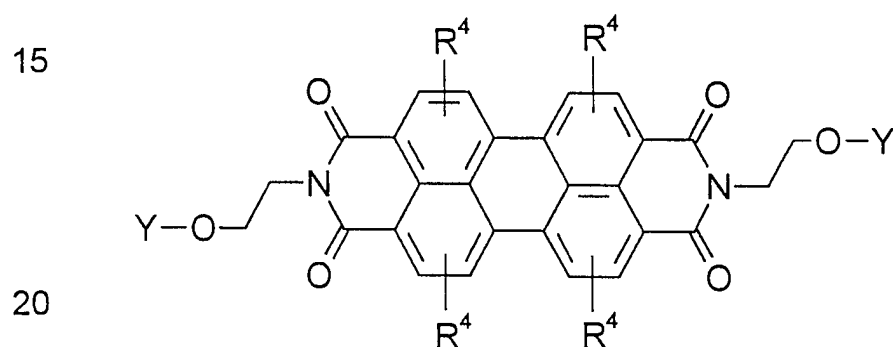
fluorescein-5-maleimide,

derivatives of 2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPPD),



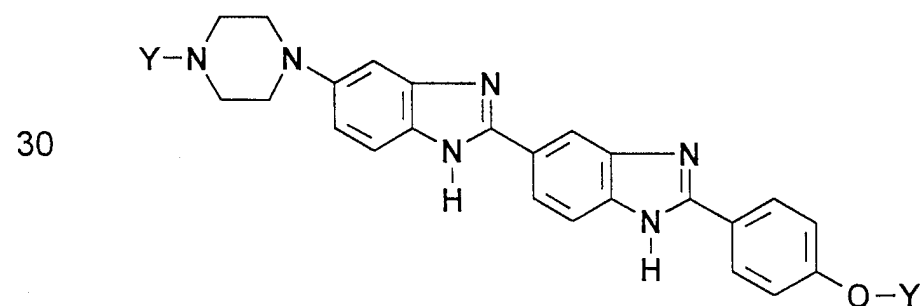
10 wherein A' has the meaning given in formula IIIA,

perylene derivatives, such as



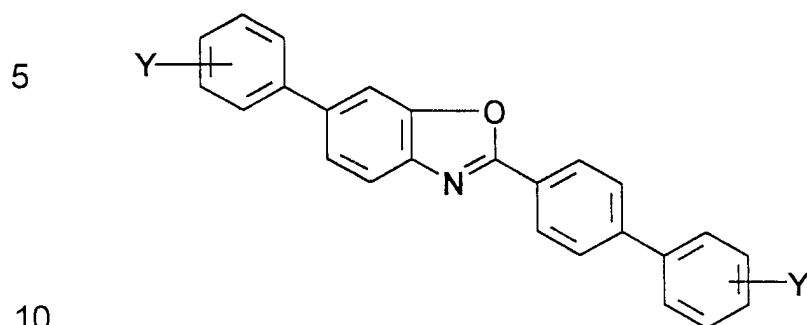
substituted 2,9-di(2-hydroxyethyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetrone, wherein R⁴ has one of the meanings of formula IIIB,

25 benzimidazole derivatives, such as



35 a derivative of 2'-(4-oxy-phenyl)-5-(piperazin-1-yl)-1H,1'H-[2,5']bibenzoimidazol, which is commercially available as Hoechst 33342 (Kodak),

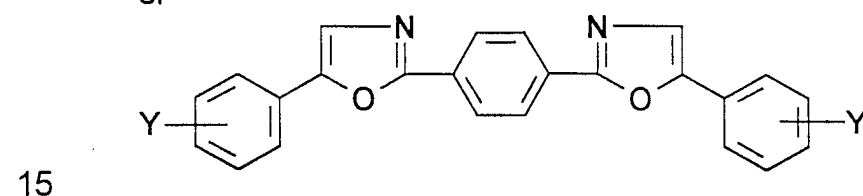
benzoxazoles, like e.g.



2-(4-biphenyl)-6-phenylbenzoxazole (PBBO)

10

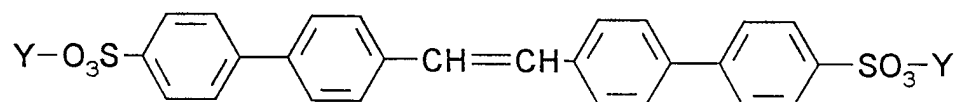
or



POPOP,

stilbenes, such as

20

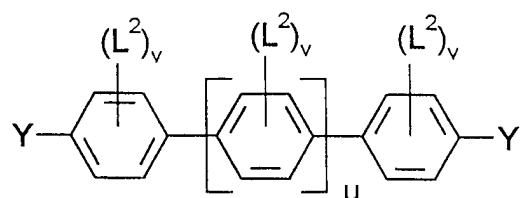


4,4'-bis-(p-sulfo)stilbene,

25

polyphenylenederivatives

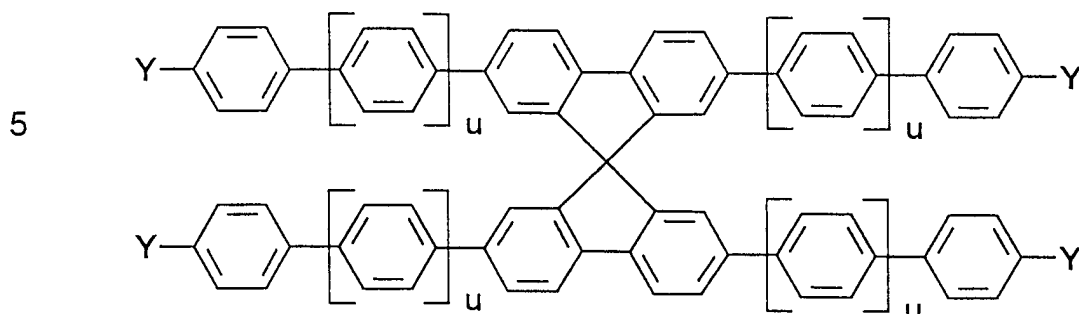
30



35

wherein u is 2 to 4, L^2 is H or C_{1-8} alkyl or alkoxy and v is 1 to 4,

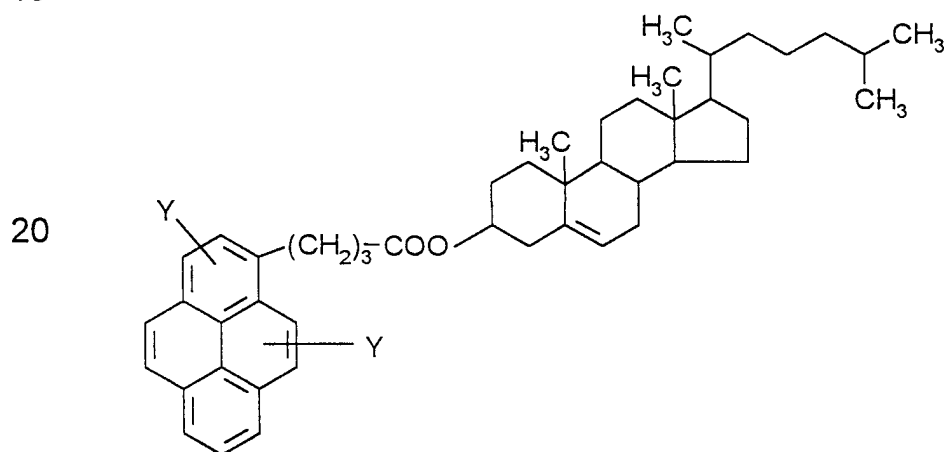
and their spiroanalogues, like



wherein one or more phenylene rings can be mono- or polysubstituted by L^2 as defined above, and u has the meaning given above,

or dyes comprising cholesteryl groups, like e.g.

15



cholesteryl-1-pyrenedecanoate.

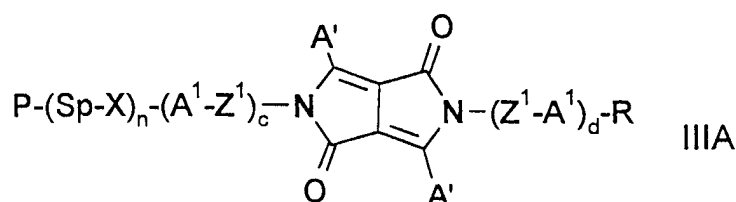
The polymerizable mesogenic compounds of formula I and I* as disclosed in the foregoing and the following can be prepared by methods which are known per se and which are described in the documents cited above and, for example, in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart.

35

Further methods of preparation, in particular for the preparation of compounds of formula I*, can be taken from the examples.

A preferred group of polymerizable compounds of formula I* comprising fluorescent dyes are pyrrolopyrroldions of the following formula

5



10

wherein

P, Sp, X, n and R have the meaning of formula I,

15

A^1 , Z^1 , c and d have the meaning of formula III, and

20

A^1 is phenyl in which, in addition, one or more CH groups may be replaced by N, cyclohexyl in which, in addition, one or two non-adjacent CH_2 groups may be replaced by O and/or S, cyclohexenyl or naphthalene-2-yl, it being possible for all these groups to be unsubstituted, mono- or polysubstituted with halogen, cyano or nitro groups or alkyl, alkoxy or alkanoyl groups having 1 to 7 C atoms wherein one or more H atoms

25

may be substituted by F or Cl,

30

The pyrrolopyrroldione dyes exhibit a brilliant colour, acceptable solubility and have a low influence on the glass temperature of the polymer. Inventive pigment flakes obtained from an inventive chiral polymerizable mesogenic material comprising such dyes show particularly brilliant colour effects.

Particularly preferred are difunctional polymerizable compounds of formula IIIA, i.e. wherein R is $P-(Sp-X)_n$.

35

Further preferred are compounds of formula IIIA wherein A' is phenyl, in which one or 2 CH groups may be replaced by N, which is unsubstituted or substituted in one to four, preferably one, two or three positions by F, Cl, CN, OCF₃ or linear or branched alkyl or alkoxy with 1 to 7, preferably 1 to 4, C atoms.

5

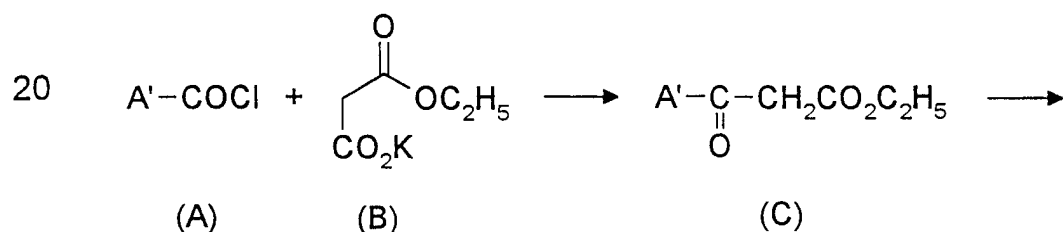
A' is particularly preferably phenyl, 3,5-dimethylphenyl, 2-methylphenyl, 4-tert.butylphenyl, or 4-methyl-, 4-fluoro-, 4-chloro- or 4-cyanophenyl.

10

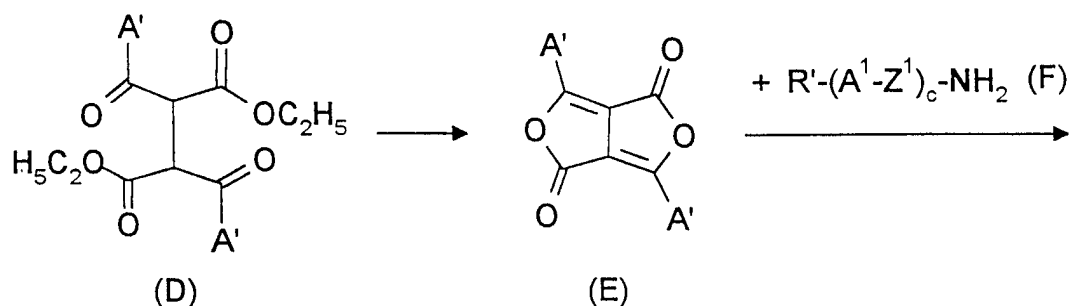
The compounds of formula IIIA can be prepared by known methods from intermediates (A) and (B) according to reaction scheme 1, wherein A', A¹, Z¹ and c have the meanings of formula IIIA and R' denotes R or P-(Sp-X)_n-. Some specific methods of preparation can be taken from the examples.

15

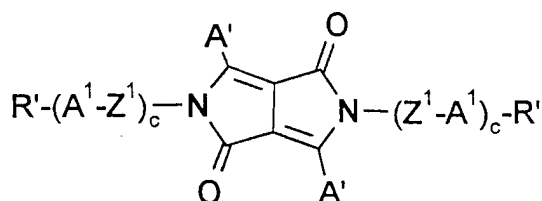
Scheme 1



25

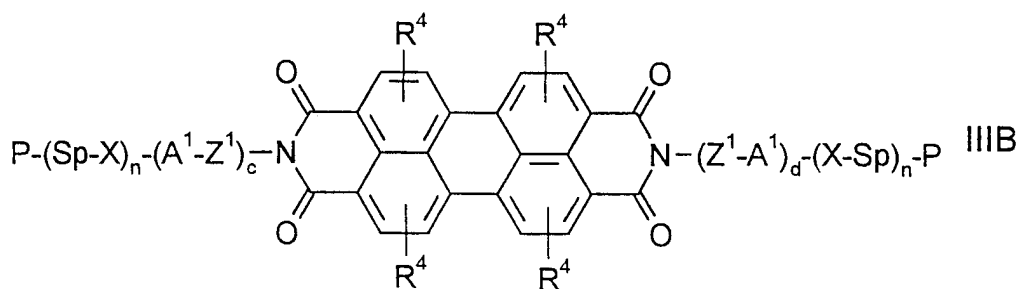


30



The starting materials (A) and (B) are commercially available and are easily transformed into intermediate (C) (for example according to the method described in Synthesis 1993, 290). (C) is dimerized into (D), which is then transformed into (E) by a procedure worked out for simple pyrrolopyrroldiones (Liebigs Ann. 1996, 679). The compounds (F) are used as precursors for the synthesis of liquid crystal azo dyes or isothiocyanates and are well known from several patents and publications, like e.g. the EP 0 250 505 or DE 40 27 869.

Another preferred group of polymerizable compounds of formula I* comprising fluorescent dyes are perylene derivatives of the following formula



wherein

P, Sp, X and n have the meanings of formula I,

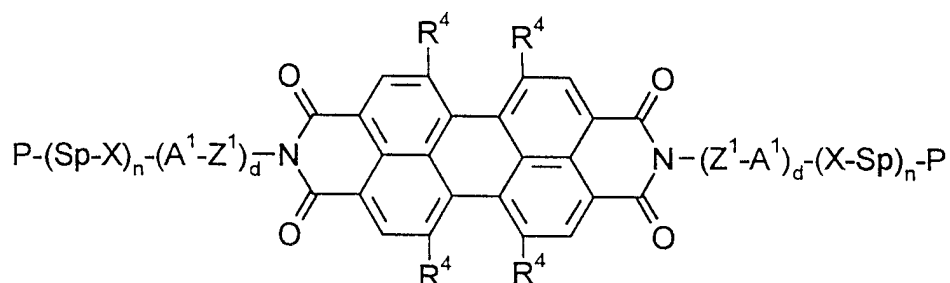
A^1 , Z^1 , c and d have the meanings of formula III, and

R^4 is denoting $-(O-Phe)_e-R^5$, with R^5 being H, F, Cl, CN, NO_2 , optionally halogenated alkyl, alkoxy or alkanoyl with 1 to 12 C atoms, Phe denoting 1,4-phenylene and e being 0 or 1.

Particularly preferred are compounds of formula III B wherein R^4 is H.

Further preferred are compounds with the following substitution pattern of R^4

5



10

R^4 in these compounds is preferably F, Cl, alkyl or alkoxy with 1 to 8 C atoms or O-Phe.

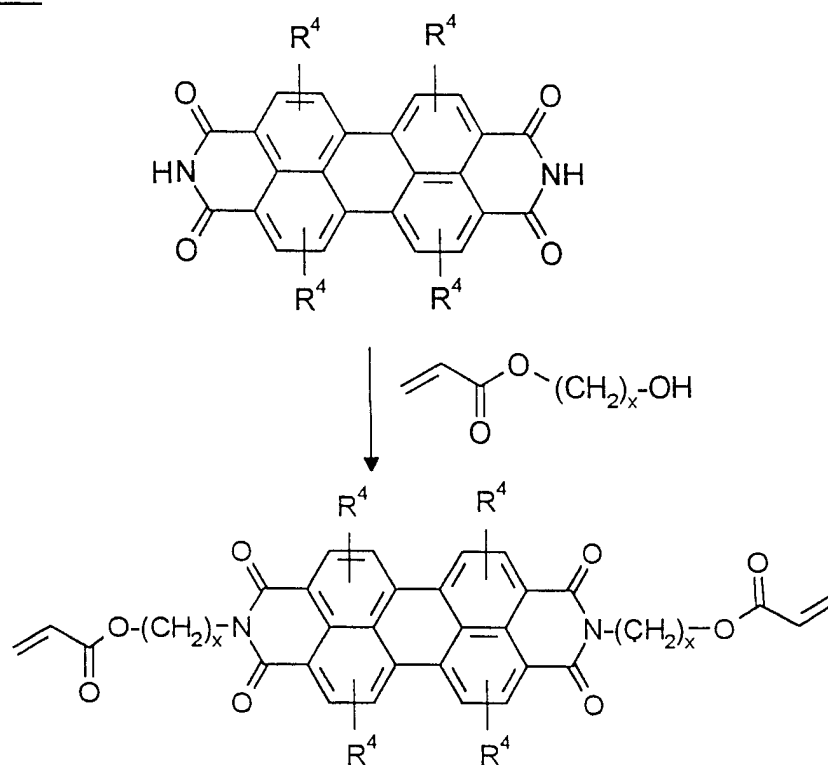
15

The compounds of formula IIIB can be prepared by known methods according to the following reaction schemes, wherein x is 1 to 8 and Sp , A^1 , Z^1 , c and d and R^4 have the meaning of formula IIIB. Some specific methods of preparation can be taken from the examples.

20

Scheme 2

25

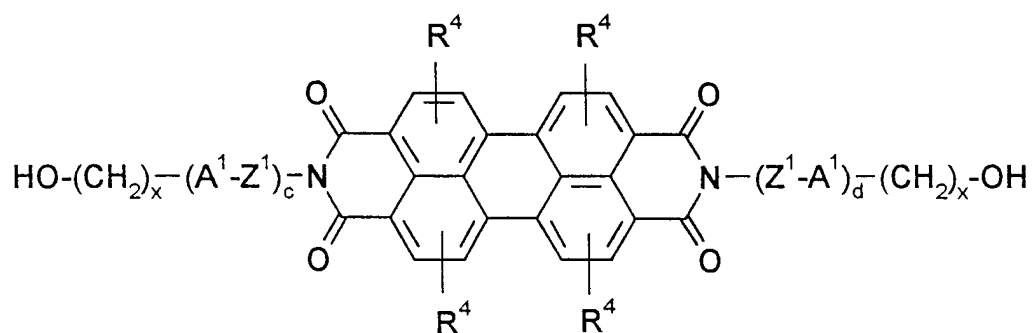


30

35

Scheme 3

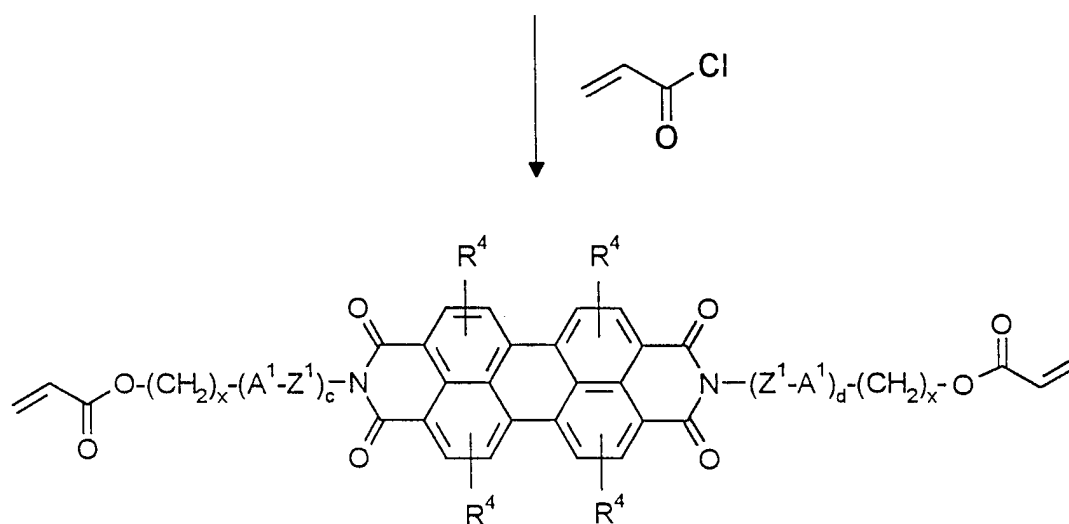
5



10

15

20



25

The compounds of formula IIIA and IIIB are new and are another object of the present invention.

30

In a preferred embodiment of the present invention, the pigment flakes are obtainable from a chiral polymerizable mesogenic material comprising the following components

- a1) at least one chiral polymerizable mesogenic compound according to formula I having one polymerizable functional group,

35

- 5
- a2) at least one achiral polymerizable mesogenic compound according to formula I having two or more polymerizable functional groups,
 - b1) at least one polymerizable mesogenic compound according to formula I* having one polymerizable functional group,
 - c) a photoinitiator, and
 - d) optionally a non-mesogenic compound having two or more polymerizable functional groups.
- 10

In another particularly preferred embodiment of the present invention, the mixture of the chiral polymerizable mesogenic material comprises

15

- a1) at least one chiral polymerizable mesogenic compound according to formula I having one polymerizable functional group,
 - a3) at least two achiral polymerizable mesogenic compounds according to formula I having one polymerizable functional group,
 - b2) at least one polymerizable mesogenic compound according to formula I* having two or more polymerizable functional groups,
 - c) a photoinitiator, and
 - d) optionally a non-mesogenic compound having two or more polymerizable functional groups.
- 20
- 25

30 The mixture according to this particularly preferred embodiment preferably comprises two to six, most preferably two to four different mesogens according to formula I having one polymerizable functional group.

35

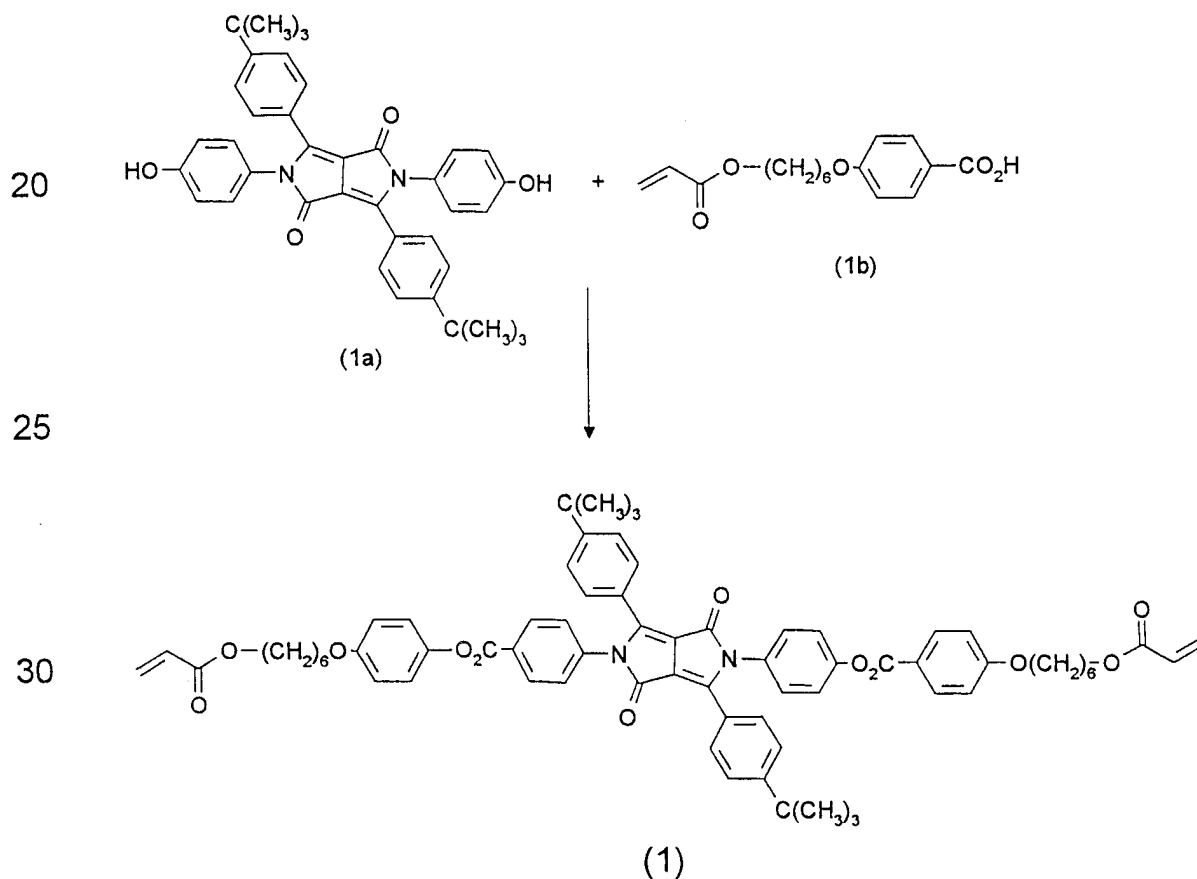
Preferably the chiral polymerizable mesogenic material comprises at least one polymerizable compound of formula I, I*, IIIA or IIIB according to one of the preferred definitions as described above.

5 A chiral polymerizable mesogenic material as described above and below is another object of the present invention.

The complete disclosure of all applications, patents and publications mentioned hereinbefore and hereinafter is introduced into this application by way of reference.

Example 1

15 Compound (1) is prepared as follows

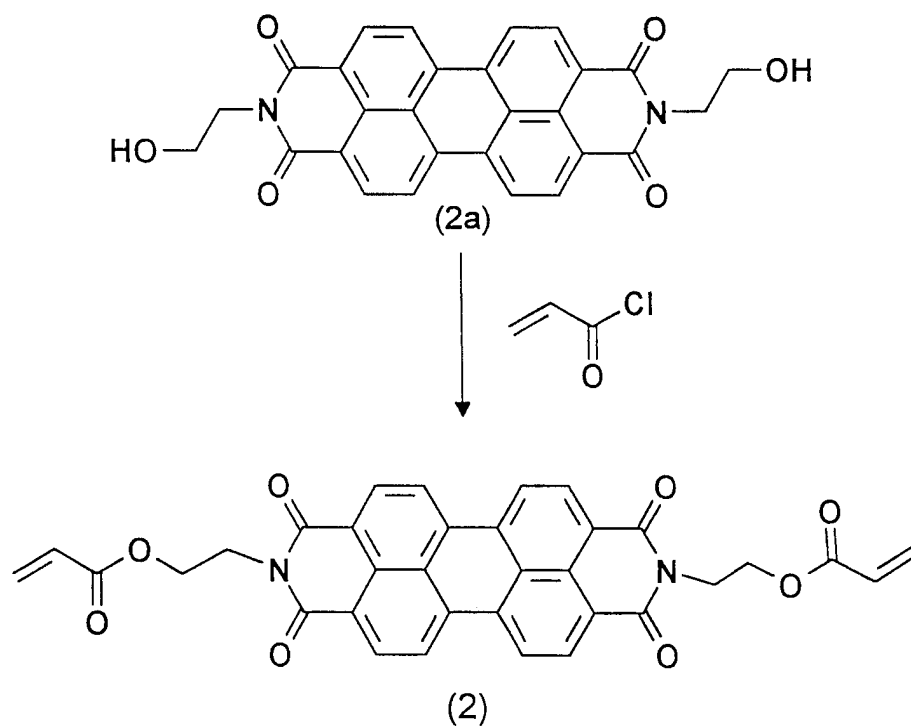


The compound is prepared analogously to a known method (Liebig's
Ann. 1996, 679) from the corresponding diketofuranofurane and
4-bromoaniline. The resulting bromoderivative is transferred via
lithiation with BuLi at - 90 °C, boronation with borotrimethylate and
oxidation with H₂O₂ to give (1a).

6,4 g of (1a), 5 g of (1b) and 0.3 g dimethylaminopyridine are
dissolved in 300 ml dichloromethane. At 0 °C to 5 °C 5.4 g
dicyclohexylcarbodiimide in 125 ml dichloromethane are added.
After stirring for 24 h at room temperature the precipitate was filtered
off and the solvent was evaporated. The residue was recrystallized
from toluene / acetone 4 : 1 to give compound (1) at a yield of 7.5 g
(red/orange crystals).

Example 2

Compound (2) is prepared as follows



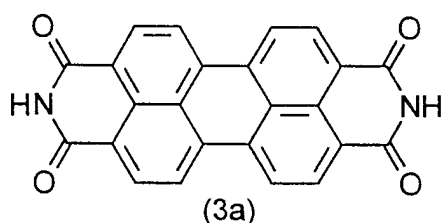
To a solution of 2.3 g (2a) (a perylene with IUPAC nomenclature 2,9-di(2-hydroxyethyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetrone, commercially available from Syntec, Germany) in 75 ml dioxane that is heated to 70 °C, 1.14 g triethylamine and afterwards 1 g acryloylchloride, each in 5 ml dioxane, are added together with a small amount of p-benziquinone to inhibit polymerisation. After heating for 1 h, the cooled reaction mixture is poured in 300 ml of water and the precipitate is recrystallized from toluene.

10

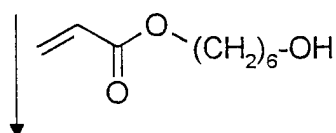
Example 3

Compound (3) is prepared as follows

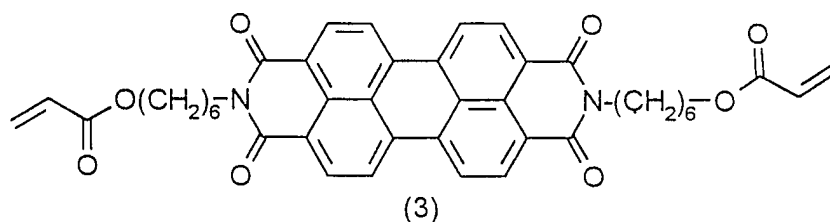
15



20



25

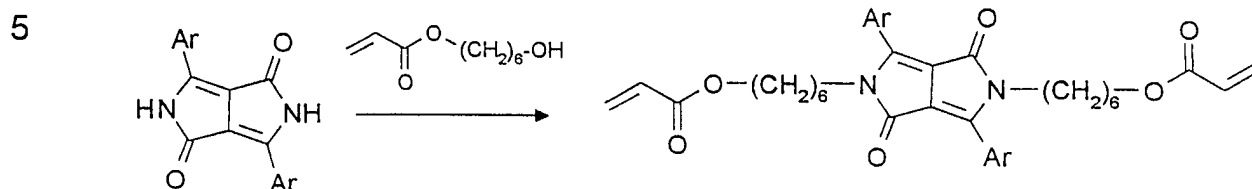


3.9 g (3a) are dissolved in 300 ml of tetrahydrofuran. This solution was added to a mixture of 2.48 g of 6-hydroxyhexylacrylate, 3.54 g of triphenylphosphine and 2.35 g of diazodicarbonic diethylester in 50 ml tetrahydrofuran containing a small amount of p-benzoquinone to inhibit polymerization. After stirring for 16 h at room temperature the solvent was evaporated off. The residue was purified by chromatography on silica gel with toluene/ethylacetate 9 : 1.

35

Example 4

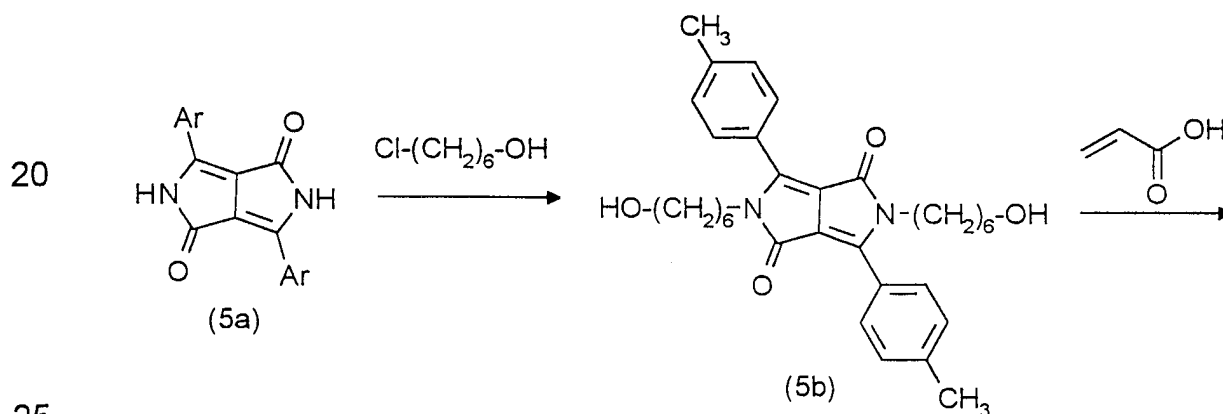
The following compounds are prepared in analogy to example 3



10 wherein Ar is phenyl, 3,5-dimethylphenyl, 2-methylphenyl or 4-t-butylphenyl.

Example 5

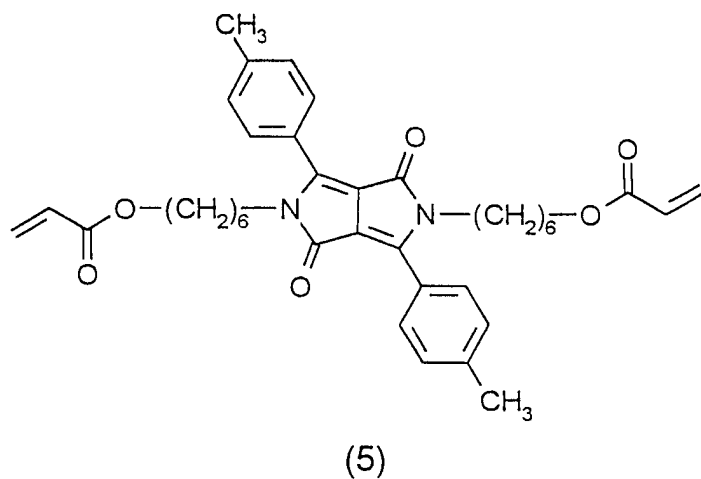
15 Compound (5) is prepared as follows



25

30

35

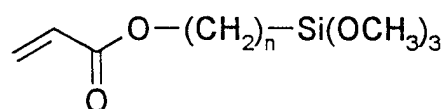


Example 7

(Modification of mica surface by wetting agent)

5 A 95 % ethanol - 5 % water solution is adjusted to pH 4,5 - 5,5 with acetic acid. The wetting silane (7) is added under stirring to give finally a concentration of 2 %. After some minutes the mica is added to the solution and stirred for 3 minutes. The particles are filtered off, washed shortly twice with ethanol and afterwards cured for 10 minutes at 110 °C.

10



(7)

15

Example 8

(Preparing the mica for alignment by rubbing).

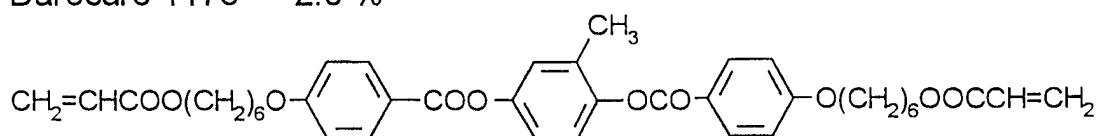
20 The surface of the mica coated with the coreactive acrylate (7) is oriented by passing it through two counter-rotating rolls covered by Nylon (Nylon YO/10N from Yoshikawa).

Example 9

25

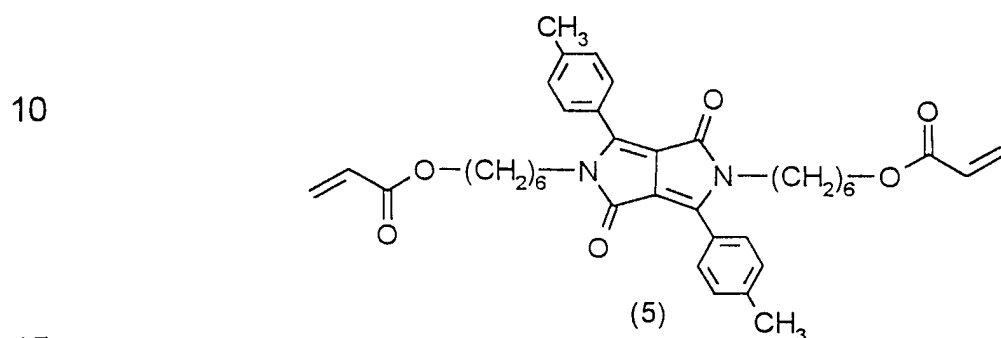
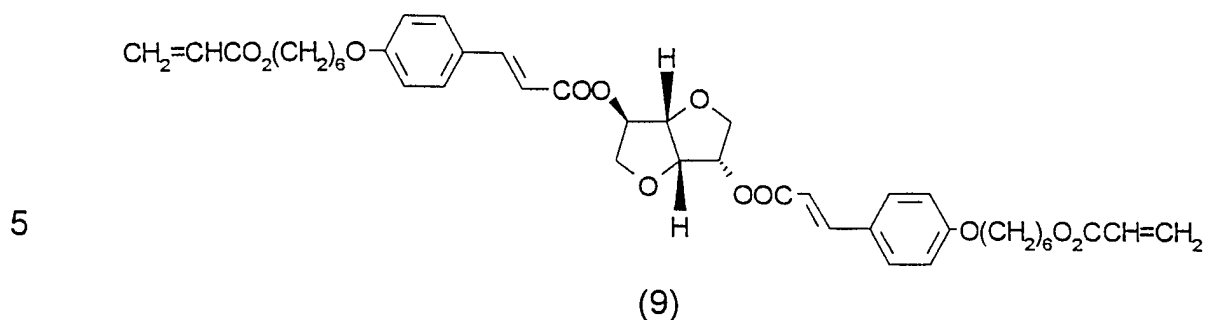
A polymerizable liquid crystalline mixture is formulated comprising the following compounds

30	compound (8)	91.5 %
	compound (9)	6.0 %
	compound (5)	0.5 %
	Darocure 1173	2.0 %



35

(8)



15
20

Compound (8) can be prepared in analogy to the method described in WO 93/22397. The synthesis of compound (9) is described in the non-published EP 96110577.2. The synthesis of compound (5) is described in example 5. Darocure is a commercially available photoinitiator from Ciba Geigy.

25

Mica particles that have been rubbed as described in example 2 are transported to a moving band made of stretched polyethylene which is covered by a thin layer of the mixture described above. The mixture is kept in its liquid crystalline phase by heating to the isotropic phase and supercooling to 60 °C. The same mixture is then sprayed in a thin layer on the upper surface of the mica flakes.

30

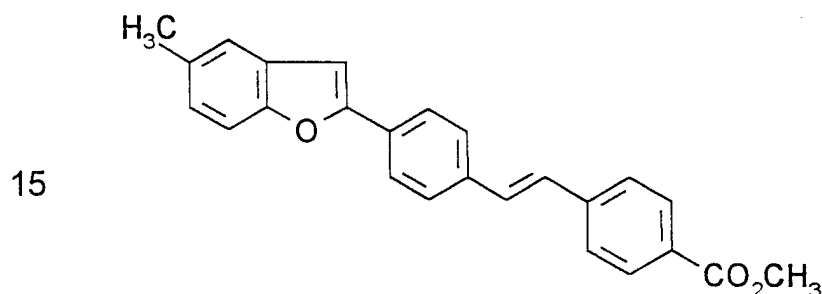
The layers are then photopolymerized by irradiation with an UV lamp (320 - 520 nm) under an argon atmosphere for five minutes.

35

After 24 hours the mica flakes are scraped off the band. They show a glossy pearlescent effect, which is varying in accordance with the viewing angle from red to a brilliant blue-green effect caused by the fluorescence of compound (5) and the cholesteric reflective effect induced by compound (9).

5 The preparation of flakes as described above can be repeated with the same or another inventive chiral polymerizable mesogenic material comprising another dye in addition to or instead of the fluorescent dye, with or without the above chiral polymerizable compounds or other chiral polymerizable compounds.

10 It is also possible to add small amounts of non-polymerizable dyes to the chiral polymerizable mesogenic material, like e.g. 0.2 to 2 % of 9,10-diphenylanthracene (from Merck), 9,10-bisphenylethynylanthracene (from Aldrich), or the following compound (from Hoechst)



in order to vary the colour effects.

20 A simple colour tuning of the coating can furthermore be achieved by applying azodyes (in the range of 0.1 % to 10 %) or other dyes like indigo as mentioned above.

25 The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

30 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

35

Patent claims

- 5 1. Pigment flakes comprising a chiral liquid crystalline polymer material, said chiral liquid crystalline polymer material serving as carrier material or being coated onto a carrier material, characterized in that the pigment flakes comprise at least one dye that is chemically bound to the polymer.
- 10 2. Pigment flakes according to claim 1, characterized in that at least one of the chemically bound dyes is a fluorescent dye.
- 15 3. Pigment flakes according to claim 1, characterized in that they additionally comprise one or more dyes or pigments which are not chemically bound to the chiral liquid crystalline polymer material.
- 20 4. Pigment flakes according to any of the claims 1 to 3, characterized in that the chiral liquid crystalline polymer material forms a three dimensional network.
- 25 5. Pigment flakes according to any of the claims 1 to 4, characterized in that they have a thickness from 0.1 to 100 μm and lateral dimensions from 1 to 1000 μm .
- 30 6. Pigment flakes according to any of the claims 1 to 5 comprising a chiral liquid crystalline polymer material, said liquid crystalline polymer material being coated onto a carrier material, characterized in that the pigment flakes are obtainable from a chiral polymerizable mesogenic material by a process comprising the following steps
 - 35 a) coating a thin layer of the chiral polymerizable mesogenic material onto the carrier material,
 - b) aligning the chiral polymerizable mesogenic material in the coated layer into a uniform orientation,

- c) polymerizing said chiral polymerizable mesogenic material by exposure to heat or actinic radiation.

- 5 7. Pigment flakes according to any of the claims 1 to 6, characterized in that mica is used as carrier material.
8. Pigment flakes according to any of the claims 1 to 5, comprising a chiral liquid crystalline polymer material, said liquid crystalline polymer material serving as carrier material, characterized in that the pigment flakes are obtainable from a chiral polymerizable mesogenic material by a process comprising the following steps
- 10
- a) coating a thin layer of the chiral polymerizable mesogenic material onto a substrate or between two substrates,
- 15
- b) aligning the chiral polymerizable mesogenic material in the coated layer into a uniform orientation,
- 20
- c) polymerizing said chiral polymerizable mesogenic material by exposure to heat or actinic radiation,
- 25
- d) optionally removing the substrate, or, if two substrates are present, one or both of the substrates from the polymerized material,
- e) grinding the polymer film into small particles of the desired dimensions.
- 30 9. Pigment flakes according to claim 6 or 8, characterized in that the chiral polymerizable mesogenic material comprises at least two polymerizable mesogenic compounds, at least one of which comprises a chromophoric group.
- 35 10. Pigment flakes according to claim 6, 8 or 9, characterized in that the chiral polymerizable mesogenic material comprises at least

one polymerizable mesogenic compound having one polymerizable group and at least one polymerizable mesogenic compound having two polymerizable groups.

5 11. Pigment flakes according to claim 6, 8, 9 or 10, characterized in that the chiral polymerizable mesogenic material comprises at least one chiral polymerizable mesogenic compound and at least one achiral polymerizable mesogenic compound.

10 12. Pigment flakes according to any of the claims 1 to 10, characterized in that they are obtainable from a chiral polymerizable mesogenic material comprising at least one polymerizable mesogenic compound of formula I*

15 $P-(Sp-X)_n-CG-R$ I*

and optionally at least one polymerizable mesogenic compound of formula I

20 $P-(Sp-X)_n-MG-R$ I

wherein

25 P is a polymerizable group,

Sp is a spacer group having 1 to 20 C atoms,

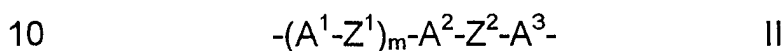
30 X is a group selected from -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -SO₂-O-, -O-SO₂- or a single bond,

n is 0 or 1, and

35 R is H or an alkyl radical with up to 25 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂

5 groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, or alternatively R is halogen, cyano or has independently one of the meanings given for P-(Sp-X)_n,

MG is a mesogenic or mesogenity supporting group of formula II:



with

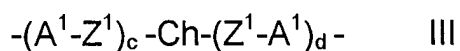
15 A¹, A² and A³ being independently from one another 1,4-phenylene in which, in addition, one or more CH groups may be replaced by N, 1,4-cyclohexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S, 1,4-cyclohexenylene or naphthalene-2,6-diyl, it being possible for all these groups to be unsubstituted, 20 mono- or polysubstituted with halogen, cyano or nitro groups or alkyl, alkoxy or alkanoyl groups having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl,

25 Z¹ and Z² being independently from one another -O-, -CO-, -COO-, -OCO-, -SO₂-O-, -O-SO₂-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond and

30 m being 0, 1 or 2,

and

35 CG is a chromophoric group or a fluorescent chromophoric group of the following formula



wherein

5

A^1 and Z^1 have the meaning given in formula II,

c and d are 0, 1 or 2,

10

Ch is denoting a chromophore or a fluorescent chromophore, which can in addition be chiral and/or mesogenic.

15

13. Pigment flakes according to claim 12, characterized in that the chiral polymerizable mesogenic material comprises at least one compound of formula I and at least one compound of formula I*.

20

14. Use of pigment flakes according to any of the claims 1 to 13 as effect pigments in printing inks, spray paints, cosmetic products or coloured plastics, active or passive optical elements or as pigments in inks and paints for security applications.

25

30

35

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/01453

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09K19/00 C09K19/38 C09B67/00 C09D5/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C09K C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	WO 97 30136 A (MERCK PATENT) 21 August 1997 see page 4, line 5 - page 6, line 19 see page 7, line 6 - page 8, line 36 see page 19, line 24 - page 20, line 24; claims 1-13 ---	1,5-8, 11,12,14
Y,P	WO 98 00475 A (MERCK PATENT) 8 January 1998 see page 6, line 17 - page 7, line 26 see page 8, line 34 - page 9, line 7 see page 9, line 28 - line 34 see page 14, line 19 - page 15, line 35; claims 1-6,11 --- -/--	1,4,6-8, 12

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
---	---

Date of the actual completion of the international search 13 July 1998	Date of mailing of the international search report 24/07/1998
--	---

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Boulon, A
--	--

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 98/01453

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	GB 2 311 289 A (MERCK PATENT) 24 September 1997 see page 1, line 5 - page 2, line 35 see page 6, line 14 - line 19 see page 15, line 9 - page 16, line 31; claims 1-11 ---	1,5,6, 11,12,14
Y	WO 96 17901 A (MERCK PATENT) 13 June 1996 see page 1, line 22 - page 4, line 35 see page 14, line 5 - line 15 ---	1,4,6, 11,12,14
Y	EP 0 171 045 A (BASF) 12 February 1986 cited in the application see page 3, line 21 - page 6, line 3 see page 8, line 23 - line 35 ---	1,2,6
Y	EP 0 260 687 A (BASF) 23 March 1988 cited in the application see page 2, line 1 - line 50 ---	1,2,6
Y	EP 0 090 282 A (BASF) 5 October 1983 cited in the application see page 1, line 4 - page 2, line 25 -----	1,2,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/01453

Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
WO 9730136	A	21-08-1997	NONE	
WO 9800475	A	08-01-1998	NONE	
GB 2311289	A	24-09-1997	NONE	
WO 9617901	A	13-06-1996	EP 0794991 A	17-09-1997
EP 171045	A	12-02-1986	DE 3429438 A JP 1916965 C JP 6043148 B JP 61064493 A US 4702945 A	23-06-1988 23-03-1995 08-06-1994 02-04-1986 27-10-1987
EP 260687	A	23-03-1988	DE 3631841 A DE 3775313 A JP 63077910 A US 4943617 A	24-03-1988 30-01-1992 08-04-1988 24-07-1990
EP 90282	A	05-10-1983	DE 3211400 A JP 58176205 A US 4631328 A	29-09-1983 15-10-1983 23-12-1986