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Optical components from a new vitrifying liquid crystal

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New low molar mass liquid crystalline vitrifying materials have been synthesized and tested for application in optical films. The molecules were based on spiro compounds derived from pentaerythritol and mesogenic groups derived from cyanobiphenylyl moieties. The resulting materials showed glass transition temperatures as high as 85°C and nematic to isotropic phase transition temperatures up to 222°C. Crystallization from the melt was strongly suppressed. Well-aligned, solid, birefringent layers were obtained from the materials by spincoating. Uniaxially oriented layers with an optic axis tilted with respect to the substrate were obtained by spincoating the liquid crystals on pretilt amplification layers. When an anisotropic dye was incorporated in the liquid crystals, polarizers with a tilted absorption axis were obtained. In addition, the compounds were found to be suitable as hosts for photo-induced reorientation of photo-isomerizable dyes.

1. Introduction

The number of plastic optical films used in active-matrix LCDs is constantly increasing [1]. Examples are brightness-enhancement films, wide viewing angle films, reflective polarizers and front-scattering films. Due to the complex optical function, these films require strict control of the microstructure. A good method for preparing birefringent films with complex optical functions is based on the photopolymerization of reactive liquid crystals [2, 3]. These liquid crystals are aligned in the desired configuration in the low viscosity monomeric state and are subsequently converted into a solid film through UV photopolymerization.

An alternative method is based on vitrifying liquid crystals with glass transition temperatures higher than room temperature. Such liquid crystals can be aligned at elevated temperatures and then stabilized by cooling below their glass transition temperatures. Liquid crystalline polymers are materials that combine liquid crystalline properties with a high glass transition temperature. Unfortunately, the high molecular mass of these materials often prevents fast, defect-free alignment. Lowering of the molecular mass will decrease the viscosity, but will also lower the glass transition temperature. However, some classes of liquid crystals combine a low molar mass with a high glass transition temperature [4]. In all cases the molecular structure is designed to suppress crystallization. Examples are: twin molecules in which two mesogenic groups are connected by a short spacer [5], spiro compounds which contain four mesogenic groups [6, 7] or cyclic compounds such as siloxanes, substituted by mesogenic groups [8]. For the applications mentioned above, materials with the highest possible glass transition temperatures (>70°C) are needed to ensure sufficient room temperature stability of the devices. Another requirement is that the materials possess a broad nematic liquid crystal mesophase above the glass transition temperature. Higher ordered mesophases are not preferred, as these phases are much more difficult to align. In addition, the materials have to be photochemically stable and transparent with respect to visible light. It has been found that most of the glass-forming liquid crystals reported in the literature do not fulfil these requirements [5–12].

In this paper we present novel low molar mass liquid crystal materials with high glass transition temperatures. The molecules are based on spiro compounds derived from pentaerythritol. These compounds seem to show a strongly suppressed crystallization [6, 7]. The mesogenic groups are derived from cyanobiphenylyl moieties. The suitability of the compounds for the preparation of birefringent foils with special optical properties has been investigated, including the preparation of retarders, compensators, polarizers with a tilted absorption axis and patterned polarizers.

2. Experimental

2.1. *Materials*

The nematic mixture E7, the anisotropic dye D2, the liquid crystalline diacrylate RM82 and 4-hydroxy-4′-cyanobiphenyl were obtained from Merck Ltd, Poole

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(GB). The photoinitiator Irgacure 651 was obtained from Ciba Speciality Chemicals. The solvents were obtained from E. Merck (Germany) and all other chemicals from Aldrich. Liquid crystal materials **1b** was synthesized as described below. All the intermediates showed NMR spectra in accordance with their supposed structures.

2.2. *Synthesis*

2.2.1. *4-(Tetrahydropyran-2-yloxy)-2-methylchlorobenzene (**2**)*

3,4-Dihydropyran (137 ml) was added drop by drop to a solution of 142.5 g of 4-chloro-3-methylphenol and 12.5 g of pyridinium 4-toluenesulphonate in 750 ml of dichloromethane, cooled in an ice bath. After the reaction mixture had been stirred for 16 h at room temperature, it was washed successively with 300 ml of semi-saturated brine and 300 ml of a 10% sodium hydroxide solution. After drying the organic layer over magnesium sulphate, the solution was passed through a 1 cm thick layer of silica and the dichloromethane and the excess of 3,4-dihydropyran were evaporated at 50°C under vacuum. The protected phenol **2** (223.5 g, 98%) was obtained as a clear oil.

2.2.2. *4-(Tetrahydropyran-2-yloxy)-2-methylbenzoic acid (**3**)*

To a suspension of 18 g of magnesium turnings and 250 ml of tetrahydrofuran were added 4 ml of bromoethane. After this mixture had been stirred for 30 min, 118 g of 4-(tetrahydropyran-2-yloxy)-2-methylchlorobenzene (**2**) were added and the mixture was heated under reflux for 24 h. After cooling, 250 ml of tetrahydrofuran were added and the mixture was cooled in an ice bath. Solid carbon dioxide was added until the exothermic reaction terminated; this was apparent from a drop in temperature to below 0°C. To the mixture were added 250 ml of diethyl ether and 1 l of water, followed by filtration to remove the excess of magnesium and separation of the layers. A 2.5M hydrochloric acid solution was carefully added to the stirred aqueous layer until the pH was 6. A white precipitate formed, which was washed with 500 ml of water and dried over silica under vacuum. Product **3** (59 g, 51%) was obtained as a white powder.

2.2.3. *4′-Cyanobiphenyl-4-yl 4-hydroxy-2-methylbenzoate (**5**)*

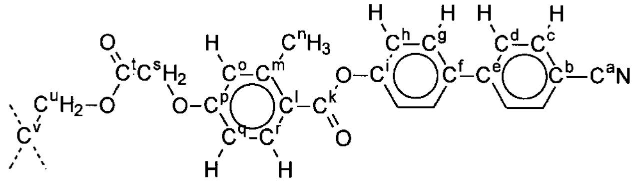
N,*N*′-dicyclohexylcarbodiimide was added, in portions (total 52 g), to a mixture of 59 g of 4-(tetrahydropyran-2-yloxy)-2-methylbenzoic acid (**3**), 49 g of 4-hydroxy-4′-cyanobiphenyl, 3 g of 4-*N*,*N*-dimethylaminopyridine and 700 ml of dichloromethane, while stirring in an ice bath. After the mixture had been stirred for one night at room temperature, it was filtered. The crude intermediate **4**, which was obtained after evaporation of the dichloromethane from the filtrate, was crystallized from approximately 1 l of ethanol. The solid was mixed with 6.2 g of pyridinium 4-toluenesulphonate and 1 l of ethanol and heated for 16 h at 60°C. After cooling, the product was collected by filtration, washed with cold ethanol and dried at 60°C under vacuum. The ester **5** (74 g, 90%) was obtained as a white powder.

2.2.4. *Pentaerythrityl tetrabromoacetate (**6**)*

A mixture of 13.6 g of pentaerythritol, 70 g of bromoacetic acid, 8 g of 4-toluenesulphonic acid and 400 ml of toluene was heated at reflux for 2 h with constant removal of water (Dean and Stark apparatus). The hot mixture was poured into a mixture of 200 g of ice and 200 ml of a 10% aqueous sodium hydroxide solution. After separation, the toluene layer was washed with 200 ml of brine, dried with magnesium sulphate and evaporated. An oil was obtained which crystallized slowly. The solid material was milled and extracted twice by stirring it with 100 ml of ethanol. The product was dried over silica under vacuum. The yield of **6** was 53 g (85%), m.p. 44°C.

2.2.5. *Pentaerythrityl tetra-[4-(4′-cyanobiphenyl-4-oxycarbonyl)-3-methylphenoxy] acetate (**1b**)*

A mixture of 44 g of 4′-cyanobiphenyl-4-yl 4-hydroxy-2-methylbenzoate (**5**), 19 g of pentaerythrityl tetrabromoacetate (**6**), 25 g of potassium carbonate and 500 ml of acetone was heated at reflux for 4 h. After evaporation of the acetone, 400 ml of dichloromethane were added and the mixture was filtered through a 2 cm layer of silica. After evaporation of the dichloromethane, a viscous oil was obtained, which was dissolved in 150 ml of acetone. After three days, the compound started to crystallize from the acetone solution. After drying at 60°C under vacuum, a yield of 24.8 g of a white solid (51%) was obtained with the following NMR data. ^{1}H (300 MHz, $CDCl_3$), δ in ppm (relative to tetramethylsilane), J in Hz: 8.17 (d, $J = 9.0$, 4H, H'); 7.71 (d, $J = 8.5$, 8H, H^c); 7.65 (d, $J = 8.5$, 8H, H^d); 7.60 (d, $J = 9.0$, 8H, H^g); 7.27 (d, $J = 9.0$, 8H, H^h); 6.82 (s, 4H, H^o); 6.81 (d, $J = 9.0$, 4H, H^q); 4.74 (s, 8H, H^s); 4.07 (s, 8H, H^u); 2.65 (s, 12H, H^n).



^{13}C (75 MHz, $CDCl_3$), δ in ppm (relative to tetramethylsilane), 167.7 (C^t), 164.8 (C^k), 160.7 (C^p), 151.3 (C^i), 144.8 ($C^e + C^m$), 136.8 (C^f), 133.8 (C^r), 132.7 (C^c), 128.4 (C^d), 127.7 (C^g), 122.6 (C^h), 121.8 (C^l), 118.8 (C^a), 117.8 (C^o), 111.5 (C_q), 111.0 (C^b), 64.7 (C^s), 62.1 (C^u), 42.4 (C^v), 22.5 (C^n).

2.3. *Methods*

2.3.1. *Preparation of films*

Solutions of compound **1b** were spincoated onto rubbed polyimide alignment layers (AL1051, JSR, Japan). Glassy films were obtained without any preferred orientation of the liquid crystal. During equilibration of these samples above their glass temperatures (120–140°C), well aligned films were obtained. Retardations were measured using ellipsometric equipment as described by Van Sprang [13]. The birefringence was determined by measuring the transmission as a function of the wavelength of a well aligned sample between two polarizers.

2.3.2. *Pretilt amplification layers*

A rigid pretilt amplification layer was prepared by photopolymerizing a liquid crystalline mixture. A rather high concentration of the liquid crystalline diacrylate (RM82) was used in combination with the commercial cyanobiphenyl mixture E7. A mixture was prepared of 30% w/w RM82, 69% w/w E7 and 1% w/w Irgacure 651. A 1% w/w concentration of the mixture in THF was spincoated onto the rubbed polyimide alignment layer and photopolymerized. Next, solutions of **1b** in THF were spincoated onto the layer, equilibrated for a few minutes at 120°C and cooled to room temperature.

2.3.3. *Dye-containing layers*

The light transmission of dye-containing samples was analysed using Autronic DMS equipment. For the photoreorientation of dyes, solutions containing 3% w/w of a 90/10 w/w mixture of **1b** and the red dichroic diazo dye D2 (E. Merck) in THF were spincoated (1000 rpm) onto polyimide substrates coated with alignment layers. The liquid crystals were aligned at 140°C and samples were exposed to linearly polarized light at 80°C. A Philips SP500 mercury lamp was used for the irradiation experiments. After exposure the samples were quenched to room temperature.

3. Results and discussion

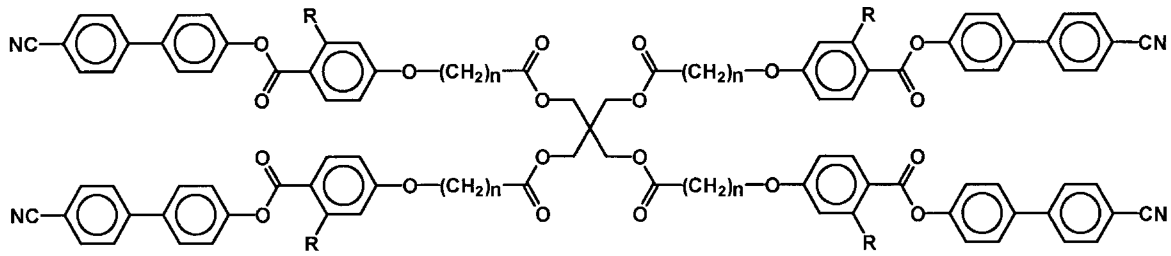
3.1. *Synthesis*

Vitrifying liquid crystals based on 4-cyanobiphenylyl groups linked to the pentaerythrityl group with the aid of ω-alkylcarboxylic acids are described in a BASF patent [7]. These materials have low glass transition temperatures and relatively low clearing temperatures. In order to increase these temperatures, we designed molecules with more complex mesogenic groups (scheme 1). In compound **1a**, the cyanobiphenylyl group was replaced by a phenylcarboxycyanobiphenyl group. From the table it is noted that this compound is smectic at lower temperatures. It also crystallizes before entering the glassy state. In order to suppress the crystallization and to lower the smectic to nematic transition temperature, a methyl group was added to the phenyl ring to obtain compound **1b**. The table shows that this compound has a glass transition in the desired range and only a nematic phase. Crystals were obtained by slowly crystallizing the compound from concentrated solutions. No crystallization from the glassy state or the nematic liquid crystalline state was observed in the case of the pure compound. In the glassy state the compound could

Table. Transition temperatures of the vitrifying liquid crystal materials (in °C).

Compound	T_g	T_m	T_t^a	T_c^b
1a	85	120	200	c
1b	78	125	—	222
1c	30	—	—	190

[a] Transition from the smectic A to the nematic phase.
[b] Transition from the nematic to the isotropic phase.
[c] Not measured due to decomposition.



1a: R=H, n=1

1b: R=CH3, n=1

1c: R=CH3, n=4

Scheme 1. Structural formulae of the glass-forming liquid crystals.

be easily dissolved in most common solvents. In the crystalline phase the compound was barely soluble.

The link between the mesogenic group and the pentaerythrityl group of compounds **1a** and **1b** was derived from acetic acid. In order to investigate the effect of a longer alkylene chain between these groups, compound **1c** was prepared, in which this link was derived from caproic acid. This compound did not crystallize either, not even from solvents. On the other hand, the glass transition temperature was too low to be of any use for our purposes.

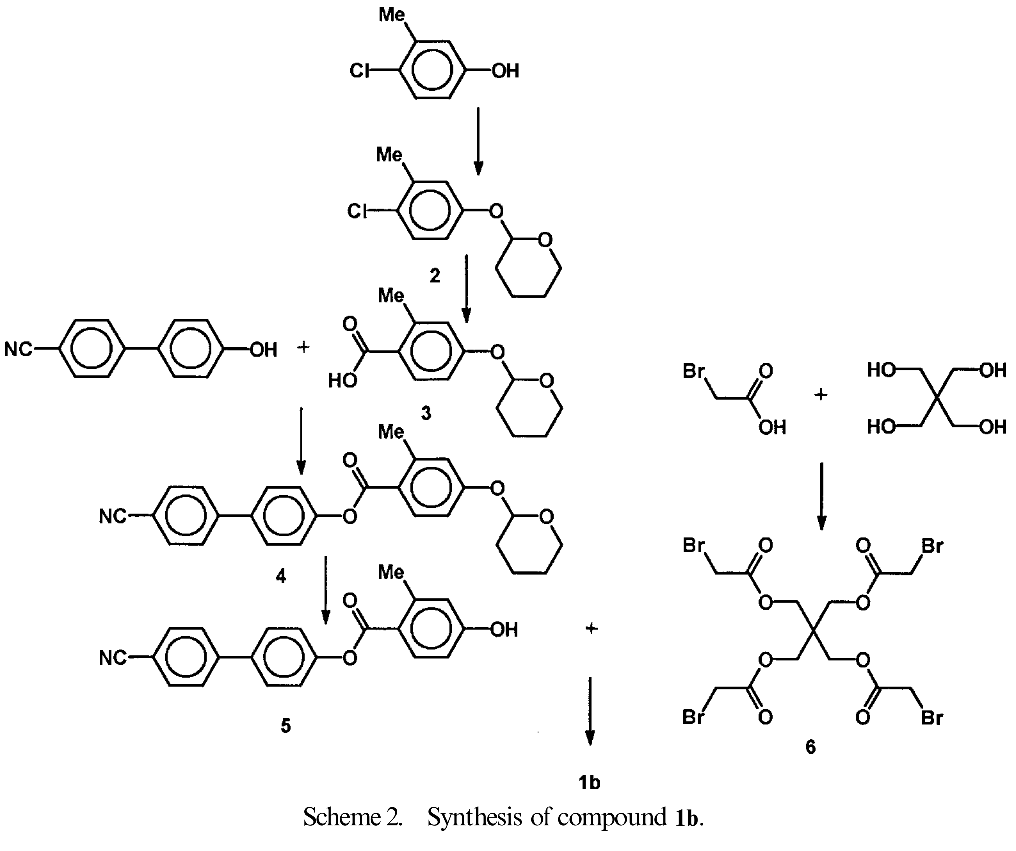
Compound **1b** was therefore the preferred compound for our experiments. Its synthesis is outlined in scheme 2. The compound was prepared by etherification of the hydroxy group of compound **5** with tetra-ester **6**, which was made by esterifying pentaeryrthritol with bromoacetic acid. To obtain mesogenic phenol **5**, the phenolic function of 4-chloro-3-methylphenol was protected as the tetrahydropyranyl ether **2**. The Grignard derivative prepared from this compound was then carbonated to form the acid **3**. Compound **5** was then prepared by deprotecting **4** which was obtained by estrifying 4′-cyano-4-hydroxybiphenyl and acid **3**. Use of the tetrahydropyranyl ether as protecting group presents the advantage that it can be used as the protecting group in both steps in which protection is required, namely the formation of the Grignard compound and the esterification. Furthermore, deprotection is much easier and can be performed under less severe conditions than when a methyl group is used as protecting group [14]. This is why the ester group is not attacked during the deprotection.

Compound **1a** was prepared in a similar fashion, by replacing acid **3** by the tetrahydropyranyl-protected 4-hydroxybenzoic acid [15]. Compound **1c** was prepared by using the esterification product of pentaerythritol and 6-bromocaproic acid instead of compound **6** in the final step.

3.2. *Optical films*

3.2.1. *Preparation of retarders*

For the preparation of optical films the birefringence of the compounds is an important parameter. Compound **1b** showed a birefringence close to 0.3 (figure 1). This high birefringence is most likely due to the high degree of supercooling of the samples at room temperature and the long rigid blocks. Because of the proximity of strong absorption bands (wavelength of maximum absorption: 276 nm), the birefringence increases rapidly on approaching the UV region. Due to the very high birefringence, thin layers made from this material will already show a high retardation.



Scheme 2. Synthesis of compound **1b**.

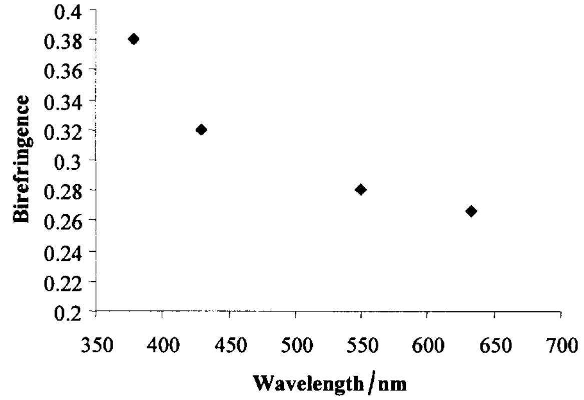


Figure 1. Birefringence of compound **1b** as a function of wavelength.

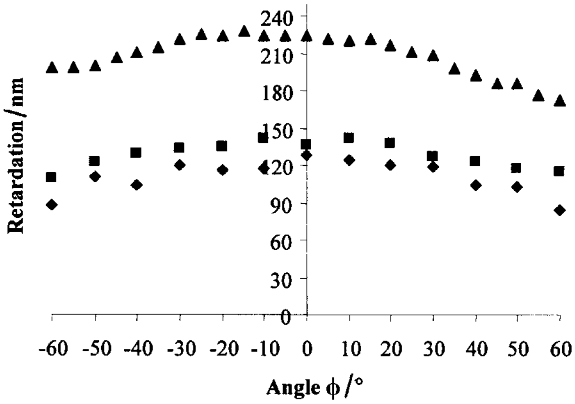


Figure 3. Retardation profiles of thin layers of **1b**.

The characteristics of spincoated films of **1b** were investigated by measuring the retardation as a function of polar angle. The retardation (R) as a function of the tilt angle (θ) of the molecules in the layer and the angle of incidence of the light (ϕ) is given by equation (1) [16]. For an explanation of the symbols, see figure 2.

$$\frac{R}{d}=\frac{n_o^2-n_e^2}{n^2}\sin\theta\cos\theta\sin\phi + \frac{n_o n_e}{n^2}(n^2-\sin^2\phi)^{1/2}-(n_o^2-\sin^2\phi)^{1/2} \qquad (1)$$

and

$$n^2=n_o^2\cos^2\theta+n_e^2\sin^2\theta.$$

This formula was fitted through the data points yielding the tilt angle of the molecules in the layer. A few examples of retardation profiles are shown in figure 3. The calculated tilt angles of the molecules in the layer correspond to the pretilt angle of the polyimide (1°). The tilt angle was independent of the thickness of the layer at thicknesses up to several microns.

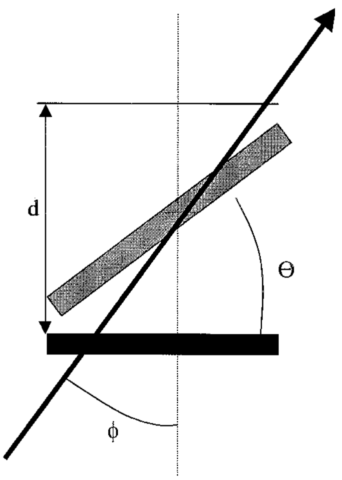


Figure 2. Symbols used in equation (1) ϕ indicates the angle of incidence of light; θ is the tilt angle of the optic axis; d is the thickness of the layer.

3.2.2. *Preparation of foils with a tilted optic axis*

Foils with a tilted optic axis are highly suitable for improving the viewing angle dependence of active-matrix twisted nematic LCDs [14, 17–21]. Foils with a tilted optic axis can be prepared from liquid crystals when the long axes of the molecules can be oriented at a high angle with respect to the alignment layer [21]. Layers with tilted mesogens can be obtained by making use of pretilt-amplification layers [22]. Liquid crystal materials containing apolar and polar moieties show a tendency towards homeotropic alignment at the liquid crystal–air interface. When a thin layer of these molecules is applied to an alignment layer, the molecules will adopt a planar orientation at the alignment layer–liquid crystal interface (figure 4). At the liquid crystal–air interface, a homeotropic orientation is desired, so a gradual planar–homeotropic transition will occur in the liquid crystal layer. The tilt angle at the liquid crystal–air interface can be proliferated in liquid crystal layers deposited on top of the amplification layer. We investigated this method using our vitrifying liquid crystals. In contrast to the retardation foils studied in [21], these foils showed a constant tilt of the optic axis in the layer instead of a gradient in the optic axis.

A rigid pretilt amplification layer was obtained by photopolymerizing a thin layer of a mixture of E7 and a liquid crystalline diacrylate. A solution of **1b** was spincoated onto the layer. A representative example of the retardation profile of such a layer is shown in figure 5. The retardation profile is asymmetric with respect to the y-axis, indicating that a tilted optic axis is present. Using equation (1), the tilt angle of this layer was calculated to be 30°. This is in the correct range for compensation foils. The tilt angle can be adapted to other values by

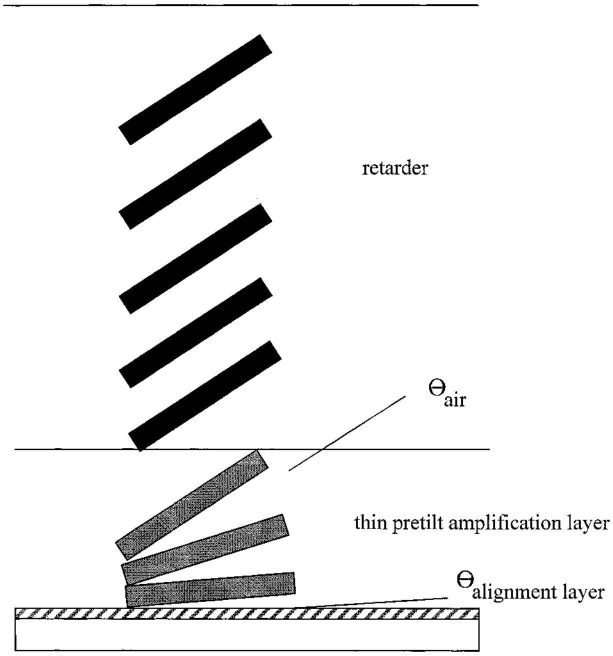


Figure 4. Principle of pretilt amplification.

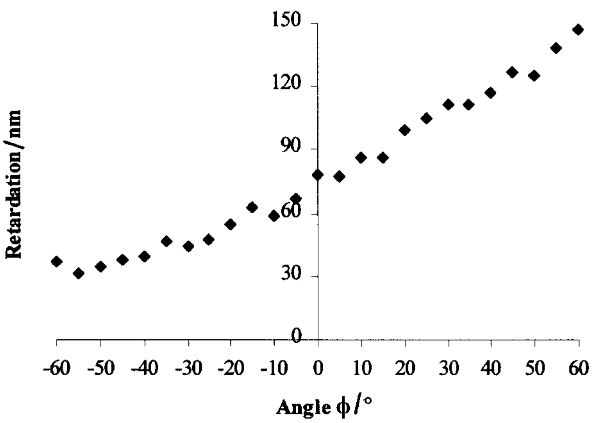


Figure 5. Retardation profile of a layer with a tilted optic axis.

optimizing the layer thickness and the composition of the mixture used for the pretilt amplification layer.

3.2.3. *Polarizers with a tilted absorption axis*

When a dichroic dye is incorporated in layers with a tilted orientation of the liquid crystal molecules, polarizers with a tilted optic axis can be obtained. Due to the relatively low order parameter of the dye in the liquid crystal the contrast ratio is limited to values of about 10. It is also possible to implement an absorption function in a viewing angle compensator. This could be useful for eliminating off-normal colouration in LCDs. At oblique angles, the absorption of light polarizer in the plane shown in figure 2 will be asymmetric with respect to normal incidence. The absorption of light passing at an angle of incidence ϕ will be lower than that of light passing at an angle of incidence $-\phi$. For light polarized in the direction opposite to the plane shown in figure 2 the absorption characteristics will be symmetric.

Solutions of mixtures of dye D2 and **1b** were deposited on a rubbed polyimide layer coated with a pretilt amplification layer. Figure 6 shows the ratio of the transmission of polarized light passing at an angle $-\phi$ to the transmission of light passing at an angle ϕ as a function of the polar angle ϕ. It is clear that the transmission characteristics of the layer spun onto the pretilt amplification layer are highly asymmetric, whereas those of the layer spun on the polyimide are symmetric.

3.2.4. *Patterned polarizers*

Wendorff and coworkers have demonstrated a method based on isomerizable dyes and polarized light to influence the orientation of dyes in polymer hosts [23, 24]. Due to the low viscosity of its nematic phase, **1b** should be very suitable for this process. Mixtures of the dye D2 and **1b** were oriented on a rubbed polyimide layer, and the dye molecules were realigned using polarized light from a mercury light source. The polarization direction was rotated 45° with respect to the original alignment direction of the liquid crystals. The samples were then irradiated at a temperature just below the glass transition temperature of the compound. At this temperature the viscosity is sufficiently low to allow rapid reorientation of the dye by the polarized light, and

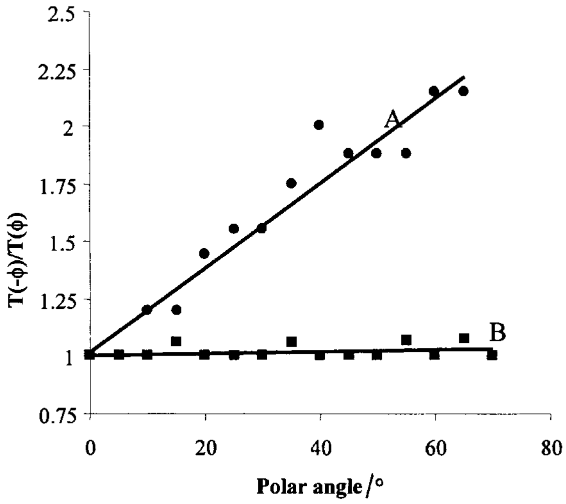
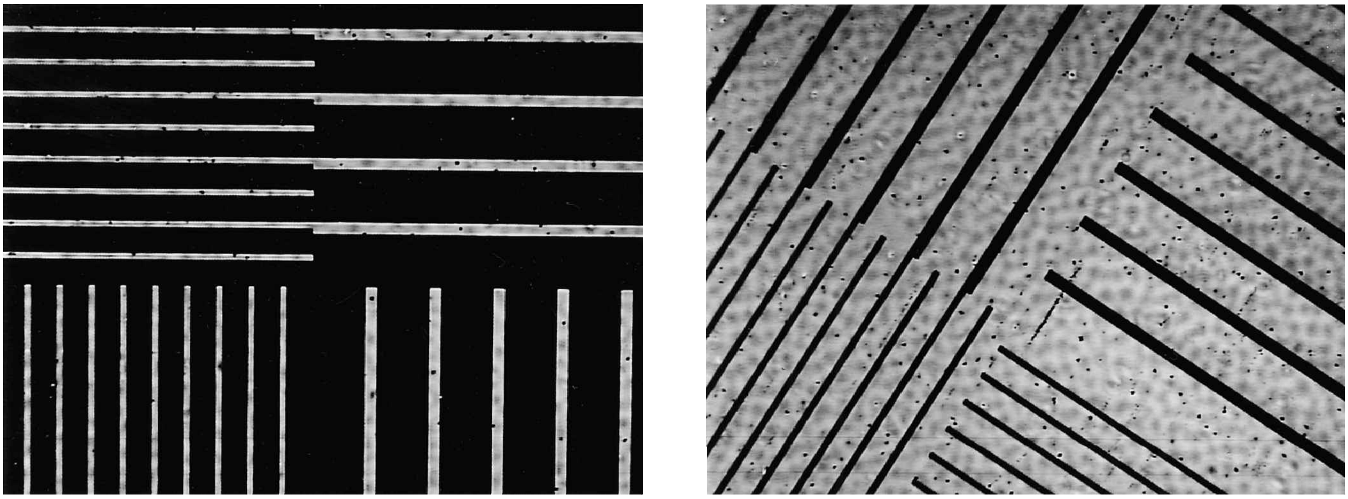


Figure 6. Transmission characteristics of dye-containing layers of a 90/10% w/w mixture of **1b** and dye D2 spun onto (A) pretilt amplification layer, (B) polyimide. The *y*-axis shows the ratio of the transmission of linearly polarized light passing at an angle $-\phi$ and the transmission of light passing at an angle ϕ. The wavelength of the light was 450 nm and the light was polarized in the plane shown in figure 2.



(*a*) (*b*)

Figure 7. Micrographs of a sample between crossed polarizers exposed patternwise to light. (*a*) rubbing direction parallel to polarizer; (*b*) illumination direction parallel to polarizer.

sufficiently high to suppress the thermally induced randomization of the orientation of the liquid crystal molecules. Parts of the sample that were not exposed to light still showed the original orientation imposed by the alignment layer. The orientation of the liquid crystal in the parts of the sample that were exposed to light was perpendicular to the polarization direction of the light. Despite the orientation direction imposed by the alignment layer, the orientation of the irradiated parts was still uniaxial (figure 7). The light transmission of the irradiated parts and non-irradiated parts between crossed polarizers was similar. This indicates that the liquid crystal molecules are also reoriented with the dye and that the order parameters of the liquid crystal material in the exposed and the non-exposed areas are similar.

4. Conclusions

Low molar mass glass-forming liquid crystals with a broad nematic mesophase range, low viscosity and high glass transition temperature have been synthesized. These materials can be used to prepare new optical components like polarizers with a tilted absorption axis and viewing angle compensators with a constant tilt of the optic axis throughout the thickness of the layer. It is considered that these materials represent a useful alternative to the method based on the photopolymerization of liquid crystals.

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