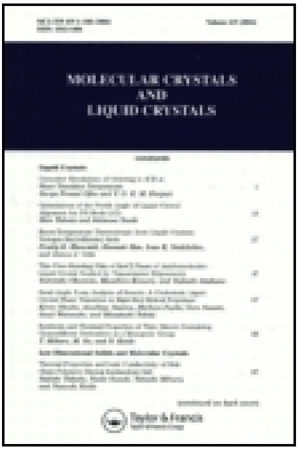

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Optical Characterization of Discotic Liquid Crystalline Films

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Optical Characterization of Discotic Liquid Crystalline Films

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We studied the distribution of optic axis and alignment of discotic molecules in discotic films with one free surface. The nematic structure of the films was fixed by photo-polymerization of discotic monomers. The distribution of optic axis within the films was studied using a null ellipsometry technique. We found that most alignment layers provide flat adhesion of the molecular discs yielding splay or homeotropic alignment of the optic axis within the film depending on the anchoring energy and concentration of polymerization agents. Two chemically modified polyimides were found to provide planar orientation of the optic axis and the molecular discs adhered with their edges to the substrate. The films can be used as optical compensation layers in liquid crystal displays.

Keywords: discotic liquid crystal; optical compensation films; photo-polymerization; alignment of discotics; liquid crystal displays

1. INTRODUCTION

Although nematic liquid crystal displays (e.g. twisted nematics, bend cells) have enjoyed greater success than other types liquid crystal displays, their introduction into certain high volume applications such as large area desktop monitors has suffered as a result of their poor viewing cone. The poor viewing angle performance and image inversion of the liquid crystal display is due to the positive birefringence of the liquid crystal layer incorporated between two polarizers. This residual birefringence produces undesirable light leakage for off-normal viewing in display modes that use two crossed polarizers in the dark state. The idea of optical compensation using passive birefringent films was developed in order to overcome this shortcoming. The ideal compensation film for producing a good dark state has negative birefringence and optic axis that mirrors that of the liquid crystal layer. One of the most promising materials for fabrication of negative films with desired optic axis distribution are discotic liquid crystals [1-4]. They possess negative birefringence with the optic axis perpendicular to the molecular plane. In order to use the discotic as a compensation layer for liquid crystal displays, one should control the alignment of its disc-like molecules. In this work, we studied the alignment of thin layers of triphenylene derivatives that show a discoidal nematic phase and the distribution of optic axis in discotic films sheared on glass substrates coated with alignment layers. The mesophases and textures of the materials used for film preparations are described in the article "Polarizing Microscopy of

Chiral Discotic" published in this journal issue. The molecular distribution in the layer was fixed by light-induced polymerization of side groups of discotic monomers within the nematic mesophase temperature range. We studied the influence of different types of alignment layers on the distribution of the optic axis in discotic films and found the conditions for planar, splay, and homeotropic alignment.

2. EXPERIMENTAL DETAILS.

In our work we studied a discotic compound from a group of 2,3,6,7,10,11 hexa-alkoxytriphenylenes (figure 2 (1,2)). The functional groups produce a wide temperature range nematic phase $T=104\text{-}180^oC$. The distribution of molecules in this compound can be fixed by polymerization of epoxide groups. Epoxides are Lewis bases and, therefore, their ring opening by cationic species, e.g. by Lewis acids, is easy. We used an Irgacure 261 photo-initiator by Ciba Additive Inc. for the photo-polymerization process. The concentration of photo-initiator was varied in the range 0.3-1%. For the films with twisted optic axis, we used a mixture of discotic compounds with epoxide functional groups (figure 1 (1,2)) and a triphenylene based discotic with the functional groups containing a chiral center (figure 1 (3)). The concentration of chiral dopant did not exceed 1.5% by weight and was adjusted to get the desired pitch according to the twisting power of the chiral discotic in the discotic matrix $\beta = 0.018\ \mu m^{-1}$.

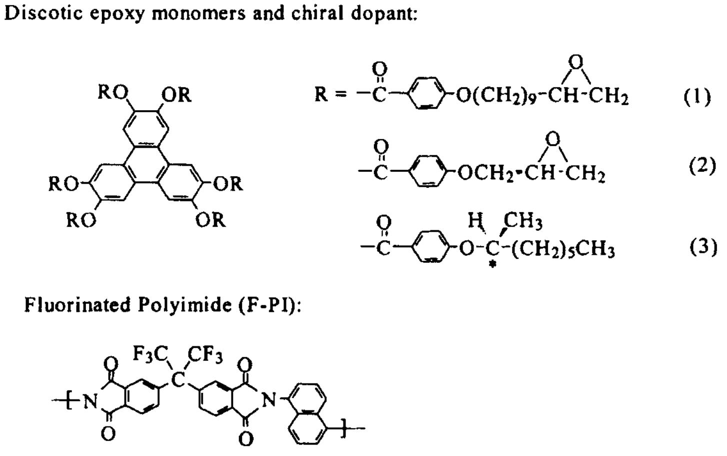

FIGURE 1. Chemical formulas of discotic compounds and fluorinated polyimide.

Discotic monomers were found to be soluble in a variety of chlorinated solvents. We used 10-20% of monomer in toluene for film casting. The films with the thickness of 1-8 microns were sheared using rods #3-10 or spin coated on substrates covered with different alignment layers. Film thickness was measured with a profilometer from Tencor Instruments. We used substrates coated with different commercial polymers: rubbed polyvinyl alcohol spin-coated on glass plates from 3% water solution, rubbed polyimides Nissan 7511 and 3510 spin coated on glass substrates using 25-30% solid in solvent and baked at 180° C and polyimide Dupont 2555 spin coated on glass plates using 25% solid in solvent and baked at 275° C. We also used a fluorinated polyimide (figure 1 (3)) spin coated on glass plates from 3.4 weight % in 1,2-dichloroethane and baked at 100° C, glass substrates treated with silanes, poly(diallyl-dimethyl ammonium chloride) (PDDA) and obliquely evaporated SiO films as an alignment layers for discotic films. After coating, the films were annealed for 5-60 min on a hot plate at 100-130°C, within the temperature range of nematic mesophase. Photo-polymerization of triphenylene epoxy monomers occurred during subsequent irradiation of the films with non-polarized UV light with a power density 27 mW/cm^2 in the wavelength range λ=320-475 nm. The exposure time varied from 200 seconds to 30 minutes.

The photo-polymerization studies were carried out using IR spectroscopy with a Nicolet Magna-IR 550 spectrometer before and after UV light irradiation. In this case, the discotic material with photo-initiator (0.5% by weight) was spin coated on NaCl plates. ^{1}H NMR spectra of monomer with photo-initiator were recorded in $CDCL_3$ solution before and after UV light irradiation using Varian Gemini-200 spectrometer.

3. STUDIES OF PHOTO-POLYMERIZATION PROCESS.

To characterize the photo-polymerization of the discotic monomer, we monitored the changes in IR spectra as a function of UV dose. No changes were detected during material heating to 130° C. However, after UV light exposure in the time interval of 200-1800 s at 130°C, a new absorption peak appears between 3300-3500 cm^{-1}. Its intensity increases with increase of exposure time. We associate this peak with the formation of O-H end-groups after ring opening of the epoxide groups.

Detailed studies of the photo-polymerization process were carried out using ^{1}H NMR. They were performed with a lower concentration of photo-initiator (0.12%) and lower intensity of the UV light source (power density 10 mW/cm^2). The studies revealed the formation of oligomeres at the beginning of the polymerization process (broad peak at 3.8-4.1 ppm, i.e. the region associated with methylene attached to oxygen)). As the polymerization progresses, a new peak appears at 5.3 ppm. It can be associated with vinyl protons attached to the aromatic ligand of the photo-initiator, i.e. new species formed after proton transfer to growing polymer chains. Both techniques confirmed that the irradiation of discotic monomers by UV light in the presence of photo-initiator induces the polymerization process.

The polymerized films were found to be insoluble in common organic solvents. Such a dramatic change in solubility supports their polymerized nature.

4.ELLIPSOMETRY TECHNIQUE.

The distribution of the optic axis in the films was studied using a null ellipsometry technique [5-6]. The measurement method is a transmission ellipsometry (polarimetry) technique featuring a polarizer and a quarter wave compensation plate fixed at 45° with respect to horizontal direction and a rotating analyzer that should be initially crossed with the polarization incident on the sample. The sample is mounted between the polarizer and the quarter wave plate with the shearing direction either in the horizontal or vertical direction. This configuration provides measurements of the phase shift between the two eigenpolarizations of the film. The light from a He-Ne laser propagating through the polarizer becomes linearly polarized at 45° with respect to the horizontal direction. The sample converts the polarization form linear to elliptical. The polarization is further transformed into almost linear polarization by the quarter wave plate. The direction of polarization of the light coming out of the quarter wave plate depends on phase shift between the two eigenpolarizations of the sample. This is determined by rotation of the analyzer to the position of minimum light leakage. In the case of normal light incidence the angle of the rotation of the analyzer φ is connected to the in-plane retardation of the sample $(n_y-n_x)d$ by the relationship $(n_y-n_x)d=\lambda\varphi/180$, where d is the thickness of the sample, n_x and n_y are two principal refractive indices for the light polarized in horizontal and vertical directions, respectively. In the case of oblique light incidence (obtained by rotating the sample about a vertical axis) the phase shift is calculated numerically from Maxwell's equations for light propagation in a biaxial medium using Berreman's 4X4 matrix method [7].

The optic axis distribution was determined under the assumption that the sample is either biaxial, with the two principal dielectric axes coincident with the plane of the film, or a stack of uniaxial films with a tilted optic axes.

5.RESULTS AND DISCUSSION.

The film textures and distribution of optic axis within the film depends on the alignment layers. We found that non-rubbed glass substrates, glass treated with silanes, lecithin and PDDA yield schlieren textures that indicate oblique alignment of the optic axis [1]. Most of the rubbed alignment layers (polyvynyl alcohol, polyimides 3510 and 2555) and obliquely evaporated SiO layers produce a uniform film with small in-plane optical retardation. However, the phase measurements confirm that they have splayed optic axis distribution. Figure 2 (a) shows curves for the phase shift φ versus the incidence angle of the testing beam θ for this type of film measured

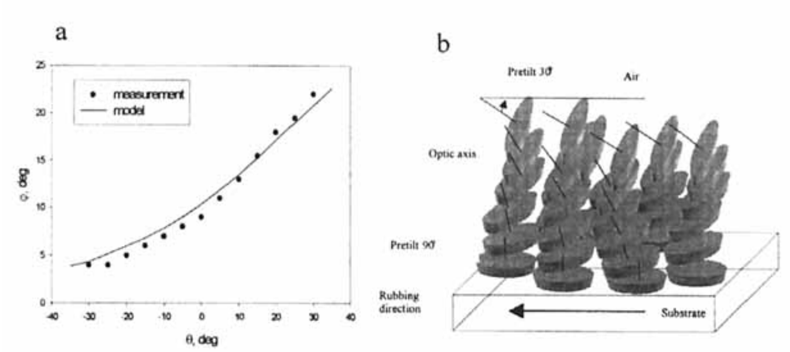

FIGURE 2. Measured and modeled φ vs θ curves for discotic splayed layer (a) and distribution of molecules in the splayed layer (b).

with its shearing direction along the horizontal. The curve is asymmetric around the head-on direction ($\theta = 0$). The phase shift between the two eigenmodes is smaller when the light propagates almost along the optic axis (negative θ) and is big when the beam is inclined to it. This suggests that the average optic axis is tilted. Detailed modeling shows that the optic axis changes its orientation from almost homeotropic near the rubbed substrate to 30° tilted at the film-air interface. The plane of splay is parallel to the rubbing direction. The projection of the optic axis is along the rubbing direction. The estimated birefringence value of the splayed films is n_o-n_e=0.04. Figure 2(b) shows the possible orientation of discotic molecules that produce this optic axis distribution. The studies show that the air interface provides high pretilt angles for the optic axis; however, the discs adhere flat to most alignment layers. We found that homeotropic alignment can be uniform within the film if the concentration of photoinitiator is as high as 1-3%. In this case the film has no in-plane retardation $(n_x$-$n_y)d=0$, however, it exhibits out-of-plane retardation $(n_x$-$n_z)d=40$-60 *nm* and n_o-n_e=0.03 where n_z is the refractive index for light polarized along the film normal. Figure 3 shows the possible alignment of discotic molecules in homeotropic films. We suggest that two processes determine the structure: the

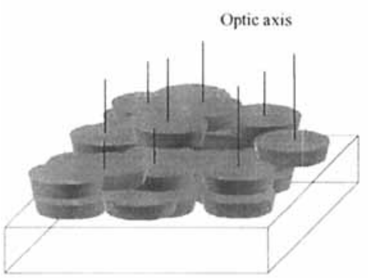

FIGURE 3. Homeotropic alignment of discotic molecules.

photo-polymerization and the anchoring. It is possible that the photo-polymerization process induces the stacking of disc-like molecules. The substrate anchoring forces the stacks to form the homeotropic structure.

We also found, that fluorinated polyimide and thin layers of polyimide 7511 provide planar alignment of optic axis of discotic films. Figure 4(a) shows φ versus θ curves for two orthogonal azimuths for the shearing direction of the planar discotic film: 1-horizontal and 2-vertical. The symmetry of the curves confirms that the three principal axes of the dielectric tensor coincide with a cartesian frame with two axes (x and y) in the film plane and one axis coincident with the shearing direction (the y-axis). The curve fitting revealed the following relationship between the three principal indices of refraction: $n_y=n_e<n_x=n_z=n_o$ and $(n_e-n_o)d= -50\ nm$. The higher in-

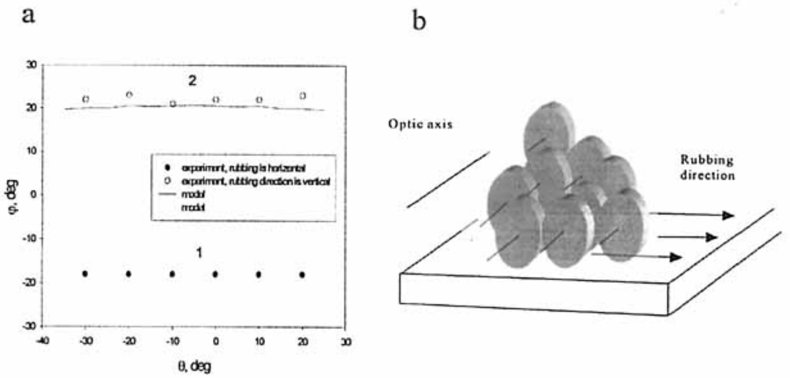

FIGURE 4. Measured and modeled φ vs θ curves for planar discotic film (a) and distribution of discotic molecules in planar film (b).

plane refractive index appears along the shearing direction. The film is negative and uniaxial with the optic axis perpendicular to the shearing direction. This relationship suggests that the discotic molecules are packed as shown in figure 4(b).

The structure can be fixed by photo-polymerization if the concentration of chiral dopant does not exceed 0.3-0.5%. The cured planar films have birefringence of n_o-n_e= *0.05-0.1* with the film thickness in the range 0.5-3 microns. The measurements obtained by ellipsometry technique agreed with refractometry measurements of the planar films performed with an Abbe refractometer. We found that the ordinary index falls in the range n_o=*1.614-1.618* and the extraordinary n_e=*1.55-1.57*. The birefringence of the film varies depending on the order parameter of each structure, giving a wider range for extraordinary index n_e than for n_o, which was nearly the same for all studied films.

The ability of some alignment layers to provide planar alignment of optic axis in discotic films allowed us to consider a negative film with twisted optic axis. The addition of a discotic dopant with chiral centers produces winding of the optic axis. The resulting textures depend on the concentration of chiral discotic and the thickness of the layer, featuring either planar alignment or fingerprints. The director twist angle in a planar film of a particular thickness is determined by the twisting power of the chiral dopant. For example, to produce a 10 μm thick film with a 90° twist that matches the birefringence of the first minimum twisted nematic cell ($\Delta nd \approx 500nm$ [8]), the concentration of the dopant should be in the range of 1.1-1.5%. However, such thick films exhibiting planar alignment and uniform twist are difficult to obtain due to the weak anchoring to the alignment layers. We obtained films with thickness up to 8 μm and twist angles 45-90°. The twist angle was estimated using a polarizing microscope. Further studies are needed in order to improve the film uniformity.

6. CONCLUSIONS.

We studied the alignment of discotic molecules on different alignment layers and found the conditions for fabrication of the negative retardation films with splayed, planar and homeotropic alignment of optic axis. The vast majority of alignment layers provide conditions for the molecular discs to adhere flat to the substrate. Two types of alignment layers (fluorinated polyimide and thin layers of polyimide 7511) provide planar orientation of the optic axis with the molecular discs adhering with their edges to the substrate. The air interface provides conditions for a tilted optic axis. The photo-polymerization of discotic monomers induces rotation of the molecular discs. The simultaneous action of processes during the photo-polymerization and anchoring forces provide the formation of tree types of structures. The most common is the splayed configuration of the optic axis featuring pretilt angles of 30° and 90° near the film-air and film-substrate interfaces, respectively. Increasing the concentration of photo-initiator to 1-3% induces the formation of structures with homeotropic orientation of optic axis. The relatively strong anchoring of rubbed fluorinated polyimide layers yields uniaxial films with optic axis perpendicular to the rubbing direction. Using the chiral discotic compound for fabrication of planar structures, we obtained films with twisted optic axis.

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