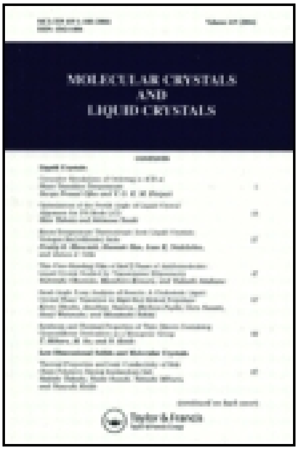

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Surface-Assisted Orientational Control of Discotic Liquid Crystals by Light

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This paper reports photoalignment control of discotic liquid crystal (DLC), a pentakis-(phenylethynyl)benzene derivative, using a thin film of an azobenzene-containing polymer. The polymer films was irradiated with non-polarized light obliquely, subsequently annealed at 240°C and coated with a DLC solution to give a mono-domain texture of DLC films with excellent optical quality. Photopatterning of DLC films was achieved by imagewise irradiation of the polymer film at an oblique incident.

Keywords: photoalignment; discotic liquid crystals; azobenzene

INTRODUCTION

Discotic liquid crystals (DLCs) are generally comprised of a disk-shaped rigid core surrounded by flexible side chains at the peripheral positions, displaying polymesomorphism such as columnar, nematic discotic (N_D), chiral discotic phase and so forth.[1] The DLCs have been attracting current interest because of their anisotropic physical properties including electronic conductivity, photoconductivity and luminescence properties. However, the progress of DLCs in quantitative researches is still limited when compared with calamitic liquid crystal (LC) systems. This is because their intrinsic properties owing to high viscosity and high mesophase temperatures lead to the difficulty in preparing well-defined textures of DLCs. In fact, there have been only few reports on the alignment control of DLCs with aid of conventional rubbed[2] and inorganic deposited[3] substrates as well as by using their freely suspended strands.[4]

Our systematic studies on the photoreactive molecular and polymeric layers for calamitic LC alignment have established that LC directors are controllable by structural as well as orientational changes of photochromic moieties including azobenzenes, which are settled on outmost substrate surfaces.[5] We have recently found that a thin film of poly[4-(4-cyanophenylazo)phenyl methacrylate] (**1**) exhibits excellent thermostability of optical anisotropy induced by linearly polarized light irradiation even after heated up to 300 °C.[6] These facts motivated us to perform the photoalignment control of DLC exhibiting a high mesophase temperature on this type of polymer thin films as a photoalignment layer.[7] Here we report the surface-assisted orientational control of a novel DLC, pentakis-(phenylethynyl)benzene derivative, with a much lower mesophase temperature (**2**)[8] (Figure 1) by placing the DLC on photoirradiated thin films of **1**.

EXPERIMENTAL

The synthesis and characteristics of **1** have been described in our previous papers.[6] Polarized microscopic observation showed that **2** posesses N_D phase between 66 °C and 84 °C.

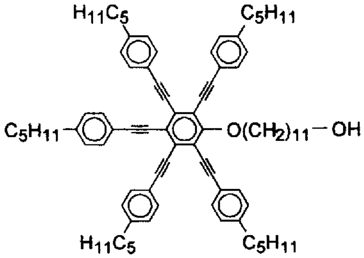

FIGURE 1 Chemical structure of a discotic liquid crystal (**2**) exhibiting N_D phase between 66 and 84 °C.

A thin film of **1** with *ca.* 25 nm thickness was prepared by spin-coating of a 1 wt.% solution of **1** in cyclohexanone on a fused silica plate. The film was irradiated with linearly polarized 436 nm light from surface normal or obliquely with non-polarized 436 nm light, followed by annealing at 240 °C for 30 min. A 20 wt.% solution of **2** in 4-methyl-2-pentanone was coated on the **1** film and evaporated to dryness to give a **2** film with *ca.* 1.0 μm, followed by heating up to the isotropic temperature of **2** at a rate of 3.0 °C min^{-1}.

Photoirradiation was performed with light from a 200 W Hg-Xe lamp through a combination of suitable filters. Optical textures of DLC films were observed by a polarized optical microscope equipped with a hot stage. Polarized absorption spectra were recorded on a photodiode array spectrophotometer (HP 8452A) equipped with a polarizer.

RESULTS AND DISCUSSION

We prepared three kinds of films of **1**, which were non-irradiated (I), perpendicularly exposed to linearly polarized light (II) and obliquely irradiated with nonpolarized light (III), in order to compare orientational behavior of the DLC.

(I) Non-irradiation of polymer 1 film

After spin-coating of the solution **2** on a non-irradiated film of **1**, an optical texture of polycrystalline structures attributed to the DLC was observed at room temperature by a polarized microscopy. When the **2** film was gradually heated up to 64 °C, the polycrystalline state was converted into a Schlieren texture attributed to N_D phase. Further heating at 76 °C even in N_D phase gave rise to the disappearance of the Schlieren texture exhibiting an optical isotropy, indicating that homeotropic alignment of DLC molecules with perpendicular orientation with respect to the substrate surface is generated.

(II) Perpendicular exposure to linearly polarized light

It is well-known that linearly polarized illumination of azobenzene-containing polymer films gives rise to molecular reorientation toward the direction perpendicular to the polarization plane of the light[9] and that the photoirradiated films generate homogeneous alignment of a layer of calamitic LC in parallel with the orientational direction of the azobenzene moieties.[10] It followed that the polarized light irradiation procedure was applied to the photoalignment of DLC.

When a **1** film was exposed to linearly polarized 436 nm light at a 3.0 J cm^{-2} dose from the surface normal, photoinduced dichroism was generated. A dichroic ratio defined as $DR = (A_\perp - A_{//})/(A_\perp + A_{//})$ was estimated to be 0.08; whereas $A_\perp$ and $A_{//}$ correspond to absorbances perpendicular and parallel to the electric vector of the actinic polarized light, respectively. The results suggest that the azobenzene orient perpendicularly to the polarization plane of the light through the photo-reorientation. Annealing at 240 °C for 30 min generated $DR = 0.35$ due to strong dipole-dipole interactions among the cyanoazobenzene residues. Subsequently, a DLC film of **2** was coated on the film of **1** and heated at an N_D phase temperature. It was revealed unexpectedly that the DLC film displays a random planar orientation at N_D phase so that linearly polarized photoirradiation of azobenzene-containing polymer films results in no controllability of DLC alignment.

(III) Oblique irradiation with nonpolarized light

We reported that the oblique irradiation of azobenzene-containing polymer thin films with nonpolarized light gives to rise to the generation of pretilt angles of calamitic LCs[11] since the molecular longitudinal axis of azobenzenes reorients towards the propagation direction of actinic light as a result of the repetition of photoisomerization and photo-reorientation to minimize the light absorption.[12] We applied herein this nonpolarized light irradiation technique to the DLC alignment control. Oblique irradiation of a film of **1** with nonpolarized 436 nm light of 3.0 J·cm^{-2} gave rise to

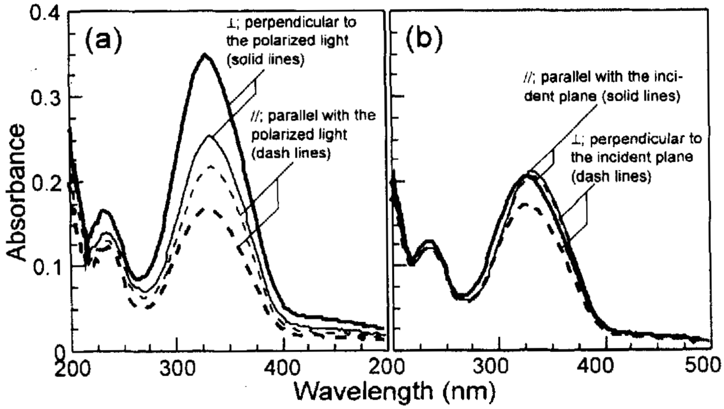

FIGURE 2 Polarized absorption spectra of polymer **1** thin film after perpendicularly irradiation with linearly polarized 436 nm light (a, thin lines) and obliquely irradiation with nonpolarized light (b, thin lines), followed by annealing at 240 °C for 30 min (a & b, thick lines).

reorientation of the azobenzene, the direction of which was in parallel with the incidence plane of the light. A *DR* value of 0.01 of the film was considerably enhanced by the annealing at 240 °C for 30 min to give *DR* = 0.09 [Figure 2 (b)].

A solution of **2** was cast on the photoaligned film of **1** to give a DLC film, and the sample was heated. It was found that the initial polycrystalline texture of DLC **2** before the heating is transformed a mono-domain texture with an excellent optical quality at N_D phase. The results show that the combination of the oblique irradiation and annealing of a film of **1** leads to the generation of mono-domain alignment of **2**, even though the photodichroism (*DR* = 0.09) of the polymer film of **1** was much smaller than that (*DR* = 0.35) induced by the perpendicular irradiation with to linearly polarized light, as given in Figure 2. It was found that the optical anisotropy of photoaligned **2** film can be preserved even at room temperature by putting on a plate at 20 °C for rapid cooling. Birefringence measurements of the photooriented film of **2** revealed that the inclined direction of DLC orientational director is opposite to the incidence direction of the nonpolarized light.[7] The surface-mediated photocontrol of DLC alignment was attainable also by the oblique exposure of a film of 1 with nonpolarized ultraviolet light (365 nm) instead of the 436 nm light.

Oblique illumination with nonpolarized light is a promising procedure to regulate both azimuthal and polar angle orientations of the azobenzene chromophores, while the irradiation with linearly polarized light from the surface normal brings about solely the azimuthal reorientation. In this context, the three-dimensional photocontrol of azobenzene orientation induced by oblique exposure is the prerequisite for the photogeneration of DLC alignment.[7]

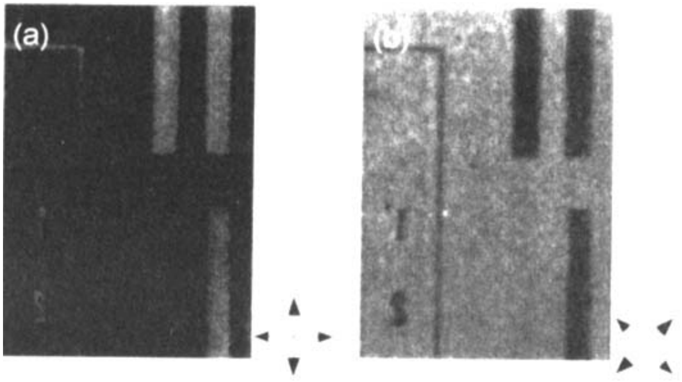

FIGURE 3 Polarized micrographs of a patterned DLC film at N_D phase. The arrows correspond to the polarization plane of polarizers.

Photopatterning of DLC alignment

Clear photoimages of patterned DLC alignment were obtained by the following procedure. A whole area of a film of **1** was obliquely irradiated with nonpolarized light in advance, followed by the photoirradiated through a photomask after rotation of the azimuthal angle at 90°. After the annealing of the film, a DLC solution was coated on the photoaligning film. Heating of the sample at N_D phase generated clear images of photoaligned DLCs under crossed-Nicol, as shown in Figure 3. A black and white images with high resolution of a micrometer scale was reversed by rotating the crossed polarizers at 45°, pronouncing that the patterned birefringence in the DLC film results from the transfer of the photooriented state of azobenzene residues as latent photoimages.

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