Polarized Photoluminescence from Photopatterned Discotic Liquid Crystal Films

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Received November 20, 2000
Revised Manuscript Received March 19, 2001

The discovery of discotic liquid crystals (DLCs)[1] has led to novel findings of other kinds of chemical structures[2] as well as their unique physical properties.[3−6] The DLCs are mostly composed of a π-conjugated central core substituted with several flexible chains at its peripheral positions to give rise to mesophases as columnar and nematic phases. The columnar phase has a long-range transitional periodicity of two dimensions as a result of intermolecular stacking among the DLCs, whereas the discotic nematic (N_D) phase possesses solely an orientational order of parallelism with respect to the DLC plane.

The orientational control of liquid crystals is highly required not only to comprehend the correlation of their orientational order with emerged anisotropic properties but also to optimize performances of molecular devices using LC systems.[7] There have been extensive reports on the orientational control of calamitic liquid crystals (CLCs) by mechanical rubbing as well as photoalignment technique,[8] leading to their versatile applications such as the display devices. In contrast, a few reports have been made on ordered and organized DLCs by surface-assisted alignment as Langmuir−Blodgett films,[9] self-assembled monolayers,[10] deposited substrates,[11] the drawing method,[12] and the external field effects of magnets[13] and lasers.[14] In this context, the current situation seems to result in the research progress of DLCs to be behind that of CLC systems. This is probably due to the difficulty in preparing well-defined DLCs because of their intrinsic properties of high viscosity and high mesophase temperature arising from strong intermolecular interactions among the discomesogens. We report here the first observation of polarized photoluminescence (PL) from a micropatterned film of DLCs, as shown in Figure 1, which was fabricated by the photoalignment technique using an azobenzene-containing polymer thin film. The spatial orientation of photoaligned DLCs in their bulk films and in their interfacial region was elucidated by ellipsometric and PL measurements.

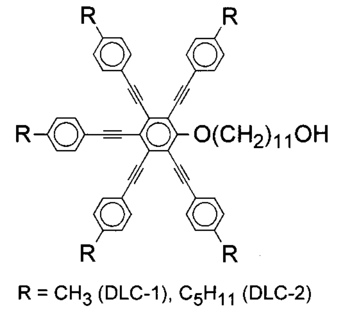

Figure 1. Chemical structures of DLC-1 and DLC-2 showing an N_D phase in the range of 172−215 and 66−84 °C, respectively.

A poly[4-(4-cyanophenylazo)phenoxy methacrylate] (**1**; $M_w = 4.3 \times 10^4$, $M_w/M_n = 3.3$, and $T_g = 185$ °C) exhibiting semicrystallinity[15] was employed to achieve orientational control of DLCs. A thin film of **1** with 25-nm thickness, prepared by spin-coating of its 1.0 wt % solution on a silica plate, was obliquely exposed to nonpolarized 436-nm light of 3.0 J cm^{-2} dose at an incident angle of 45° to generate photodichroism, followed by annealing at 240 °C for 30 min to enhance the anisotropy due to the strong dipole−dipole interactions among the *p*-cyanoazobenzenes.[16]

The level of spatial orientation of the azobenzenes induced by oblique illumination was evaluated by a dichroic ratio (*DR*)[17] as a function of incident angles (θ_m) of probing light.[18] Figure 2a shows *DR* values of a film

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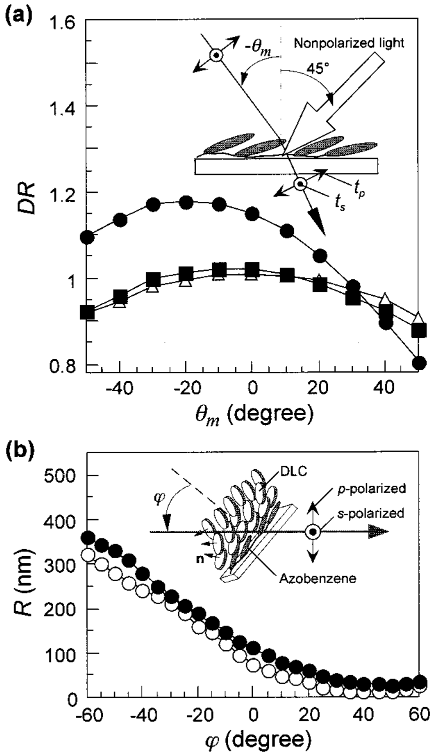

Figure 2. (a) Changes in *DR* of a thin film of **1** as a function of incident angle (θ_m) of monitoring light before (open triangles) and after (closed squares) oblique irradiation with nonpolarized 436-nm light and after subsequent annealing at 240 °C (closed circles). Inset: The experimental configuration of oblique irradiation of a **1** film with nonpolarized actinic light (open arrow). t_p and t_s stand for probing light (thin arrow) with *p*- and *s*-polarization, respectively. (b) Changes in optical phase difference (*R*) of DLC-1 (open symbols) and DLC-2 (closed symbols) glassy films as a function of incident angle of probing light (φ).

of **1** before and after the oblique exposure to nonpolarized light, followed by the annealing. A symmetrical *DR* profile with the maximum at $\theta_m = 0°$ was observed before irradiation, indicating that no orientational ordering of the azobenzenes occurs in the polar direction. The symmetrical profile arises from differences in reflectance between *p*- and *s*-polarized probing light at large θ_m. For instance, the reflection portions of 0.01% and 13% at $\theta_m = 50°$ were calculated for *p*- and *s*-polarized light according to Fresnel's equations, respectively, so that $(1 - t)$ involves both the light absorption by **1** and light reflection.[17,19] When the film was obliquely irradiated with nonpolarized visible light, the *DR* profile underwent a slight shift of the maximum value of $\theta_m < 0$. When the exposed film was subsequently annealed at 240 °C, the asymmetric profile was enhanced to give clearly the maximum *DR* value at $\theta_m = -20°$. The orientational direction of the azobenzene was aligned toward the actinic light propagation to generate a pretilt angle of ca. 20° or less.

Two pentakis[(4-alkylphenyl)ethynyl]benzene derivatives (DLC-1 and DLC-2)[20] were employed here to elucidate orientational behavior of the DLCs spin-cast on the film of **1**, which was obliquely irradiated, accompanied by annealing in advance. Polarized microscope observations revealed that DLC-1 and DLC-2 showed a N_D phase in the range of 172−215 and 66−84 °C, respectively. The temperature dependence of azimuthal retardation (*R*) was observed for a film of either DLC-1 or DLC-2 of 1.0 μm in the thickness on the polymer film by using a transmission ellipsometer[21] equipped with a hot stage according to our previous paper.[22] Before heating, each DLC film showed no optical anisotropy due to polycrystalline structures. When a DLC film was heated at a rate of 3.0 °C min^{-1}, *R* of the DLC film appeared at temperatures close to their *K*-to-N_D transition. The emerged *R* of the DLC-1 and DLC-2 films began to decline at 186 and 66 °C, respectively, and eventually disappeared thoroughly above their clearing temperatures. Once the films cooled from the isotropic phase, the *R* values revived at around their *I*-to-N_D transition temperatures and increased, even below their N_D-to-*K* points. The maxima of the *R* values upon cooling were almost 3 times larger than those upon heating. The hysteresis of thermally induced birefringence suggests that the orientational control of DLC alignment preferably occurs upon cooling from the isotropic phase. Though the optical anisotropy disappeared thoroughly at their crystalline phase upon slow cooling at a rate of 3.0 °C min^{-1}, it was found that the DLC alignment at the N_D phase could be preserved, even at room temperature, by supercooling. This is due to the formation of a glassy mesophase, which provides conveniently oriented DLC films exhibiting optical anisotropy at room temperature.

To evaluate three-dimensional orientation of the glassy DLCs film, we measured *R* values of the DLC films as a function of incident angle (φ) of probe light from the surface normal. As shown in Figure 2b, asymmetrical plots of the *R* were observed for the glassy DLC-1 and DLC-2 films, indicating the tilted alignment of DLCs despite DLCs exhibiting preferably homeotropic alignment.[3,5] Oblique exposure of the **1** film generated the tilt alignment of DLCs as a result of three-dimensional orientation of the azobenzene side chains. The average pretilt angles of both DLC-1 and DLC-2 were estimated to be ca. 70° from the substrate surface by the measurements of retardation as a function of rotation angle (φ) of the cells, as shown in Figure 2b.[16a] It is plausible that the tilt angles of DLCs are distrib-

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[17] We employed here a dichroic ratio (*DR*). The *DR* value is defined here as $DR = (1 - t_p)/(1 - t_s)$, where t_p and t_s stand for transmissions at maximum absorption wavelength due to $\pi-\pi^*$ transition of the *E*-azobenzene moieties when *p*- and *s*-polarized probing light are set at an incident angle (θ_m), respectively.

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[19] When the profile of *DR* values before irradiation was corrected by taking account of the reflection of *p*-polarized and *s*-polarized probing light, the symmetric curve was broadened. The result suggests that in-plane orientation of azobenzenes in the film has taken place already after spin-coating or that the spectral analysis has contained experimental errors due to multiple reflection of the probing light. We could not determine at present which one plays a predominant role so the original experimental data has been shown here.

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[21] The polarization-modulating transmission ellipsometer with high-optical sensibility consists of a probing He−Ne laser beam and a photoelastic modulator (PEM), leading to convenient measurements of the optical phase difference in degree unit (Δ). The Δ represents the difference of optical phase velocity between *s*- and *p*-polarized light with respect to a DLC film ($\Delta = \Delta_s - \Delta_p$), and the retardation in nanometer unit (*R*) has been calculated according to the equation of $R = 633 \times \Delta/360$.

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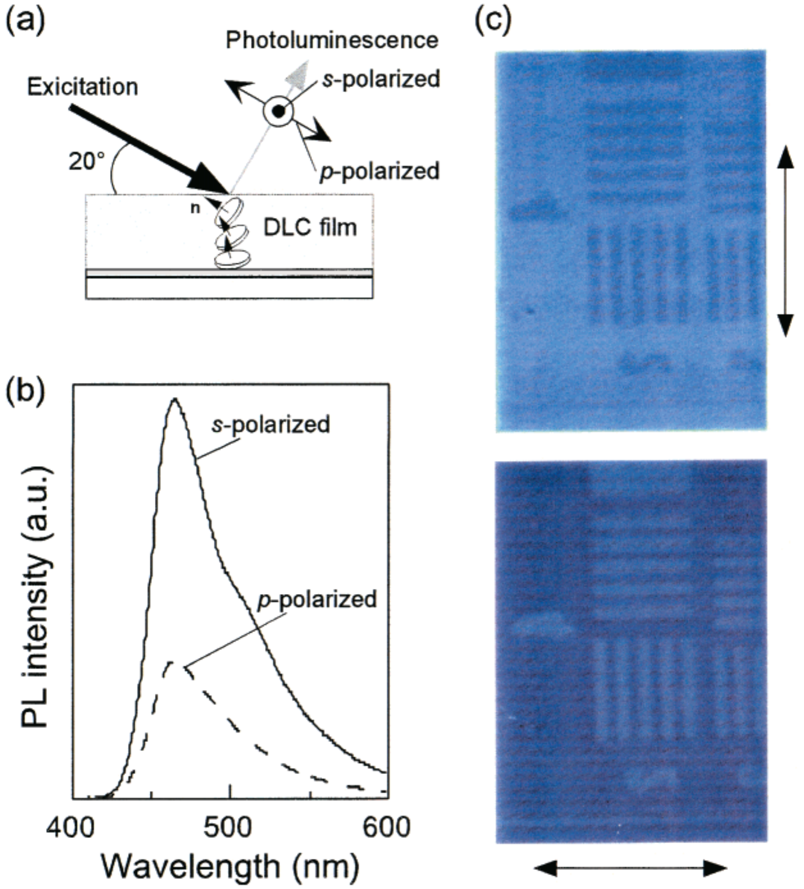

Figure 3. (a) Experimental configuration for polarized PL spectroscopy of a photooriented DLC film. (b) Polarized PL spectra of a glassy DLC-1 film by excitation with nonpolarized 340-nm light. (c) Polarized PL images of a micropatterned DLC film by nonpolarized excitation for imagewise. The arrows indicate the polarization plane of the analyzer.

uted within the film thickness due to no emergence of their optical axis.[23] The directions of DLCs are continuously altered between polymer **1**/DLC and DLC/air interfaces to minimize the free energy of the outermost surface of the DLC film to give tilted hybrid alignment.

PL measurements provided novel information on aggregations as well as spatial orientations of the outmost DLC molecules at the microscopic level. The DLCs show an absorption maximum at 340 nm in the solution.[24] A maximum emission at 462 nm was observed for both glassy DLC films by excitation at 340 nm. The emission peak was red-shifted as compared with that in dilute solution (448 nm) and is attributable to the excimer formation arising from the overlapping of DLC aromatic rings even at the glassy N_D phase. The PL analysis affords the microscopic information concerning spatially photoaligned DLCs localized at the outermost interfacial region because the penetration of the excitation light at 340 nm in DLC films is limited only at an outermost layer thinner than 100 nm. The PL intensity significantly depended on azimuthal angles of the excitation light. Maximum PL intensity was observed when the excitation was carried out from the direction opposite to the incidence plane for the oblique illumination with nonpolarized light to prepare the photoaligned film of **1**, that is, from in parallel with the orientational direction of DLC, as illustrated in Figure 3a. The results suggest that the DLCs, even at the outermost surface, preferably tilt opposite to the actinic light propagation. Figure 3b shows polarized PL spectra of a photoaligned DLC-1 film under the nonpolarized 340-nm excitation,[25] whereas the incident angle of the excitation was set at 20° from the normal to be in line with the average pretilt angle of DLCs. It was found that *s*-polarized PL emits preferentially the photoaligned DLC film in comparison with the *p*-polarized one, even when the excitation was not polarized. The intensity ratio (Em_s/Em_p) of the polarized PL at 460 nm, defined as a ratio of *s*-polarized to *p*-polarized PL in the intensity, was estimated to be 3.0, indicating that the three-dimensional ordering of the **1** film is transferred to the DLCs at the outermost surface through molecular harmonization arising from the liquid crystallinity.

A prominent advantage of the photoalignment technique is to give orientationally controlled and patterned DLC films at microscopic scale. We prepared a micropatterned DLC-1 film by the photoalignment technique to observe polarized PL from the oriented DLC. In advance, a whole area of a film of **1** was obliquely exposed to nonpolarized light, followed by the oblique photoirradiation through a photomask after rotation of

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the azimuthal incident direction at 90°.[16] Then, the DLC-1 spin-coated film on the polymer film was annealed at the N_D phase and rapidly cooled at room temperature to give its glassy film in the same manner as mentioned above. Figure 3c shows PL images on the micrometer scale through a polarizer upon illumination with nonpolarized excitation. The dark and bright areas of the blue images were inverted by the rotation of the polarizer at 90°, supporting the belief that the micropatterned PL comes obviously from the photooriented DLC film. The polarized PL photoimages from the photooriented DLC film were maintained at room temperature, even after 6 months. The present DLC photoalignment technique provides a novel guideline for comprehending the molecular orientation mechanism of DLCs, leading not only to the fabrication of novel DLC devices but also to understanding of their physical properties at the molecular level.

Acknowledgment. This work was partially supported by a Grant for “Harmonized Molecular Materials” from New Energy and Industrial Technology Development Organization (NEDO). One of the authors (S.F.) would like to thank for the support of Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists during his Ph.D. studies at T.I.T.

Supporting Information Available: Thermal changes in azimuthal retardation values of the DLC films as a function of temperature upon the heating or cooling processes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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