Surface-assisted photoalignment control of lyotropic liquid crystals. Part 2. Photopatterning of aqueous solutions of a water-soluble anti-asthmatic drug as lyotropic liquid crystals†

Takenori Fujiwara and Kunihiro Ichimura*‡

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

The photocontrol of the alignment of aqueous solutions of an anti-asthmatic drug, disodium chromoglycate (DSCG), as a lyotropic liquid crystal (LLC), was performed by irradiation of a thin film of (4-phenylazophenyl methacrylate) with linearly polarised light. The addition of a non-ionic surfactant to the LLC is a necessary condition to performing the alignment photocontrol because of the generation of nematic phase. The orientational direction of molecules of the drug was perpendicular to the electric vector of the actinic light, suggesting that columnar supramolecular aggregates composed of stacked DSCG molecules align in parallel with the long molecular axis of photooriented azobenzene chromophores, which lies in an orthogonal position with respect to the electric vector of the light. A general guideline for the photoalignment control of LLC is discussed on the basis of the results for DSCG and for a water-soluble dye, C. I. Direct blue 67, reported in Part 1 of the series.

Introduction

Thermotropic liquid crystals (TLCs) have been conventionally classified into sub-groups on the basis of the nature of mesophases, including nematic, smectic and cholesteric LCs, molecular shapes, including calamitic and discotic LCs, and molecular weights, such as low-mass and polymeric LCs.[1,2] When compared with numerous works on these kinds of TLCs carried out from both fundamental and practical viewpoints, systematic studies have been required for lyotropic LC (LLC) systems, which contain large quantities of solvents and are usually not liquid-crystalline without solvents, because LLCs have been out of the main stream of LC science and technology since no practical significance has been settled on yet.[3] We have reported recently that orientational textures of LLC derived from aqueous solutions of a water-soluble diazo dye, C. I. Direct blue 67, are manipulated by a command surface made of a ultra-thin film of an azobenzene polymer by irradiation with linearly polarised light to induce photoreorientation of the azobenzene.[4] The results are of great significance from fundamental as well as practical viewpoints to open a novel research field of relatively unexplored LLCs. Since our finding of alignment photocontrol of a low-mass nematic LC by photoisomerisation of azobenzene units tethered to substrate silica plates,[5] extensive studies have been made on the following to establish a novel research field in TLC science and technology.[6] They include developments of versatile photosensitive layers acting as command surfaces, applications to TLCs other than low-mass nematic LCs, such as polymeric nematic LCs,[7] discotic nematic LCs[8] and cholesteric LCs,[9] practical application to LC-aligning films for LC display devices[6,10] and the elucidation of the working mechanism of surface-assisted LC alignment.[6] Accordingly, we have focused our efforts on reviewing the scope and limitation of the surface-assisted alignment photocontrol

of LLCs by means of command surfaces, taking systematic studies on the surface-mediated photoalignment of TLCs into consideration.[4]

LLCs have been categorised into three sub-groups exhibiting the following mesophases according to Attwood and Lydon.[11] They include amphiphilic, chromonic and polymeric mesophases. Amphiphilic LLCs are basically comprised of aqueous solutions of surfactants bearing hydrophobic long-alkyl chain(s) with a hydrophilic terminal residue to form micelles above critical concentrations. Chromonic LLCs consist of aqueous solutions of supramolecular aggregates of polyaromatic ring systems, which are anisotropic and rigid in chemical structures and substituted with highly hydrophilic residues. Polymeric mesophases emerge not only for synthetic polymers, but also for naturally occurring biopolymers such as polypeptides, nucleic acids and cellulose derivatives. Our first observation for the surface-assisted photocontrol of LLCs was made on a water-soluble diazo dye, aqueous solutions of which belong to the chromonic LCs.[4] In this context, our attention has been concentrated in this work on chromonic LLCs derived from water-soluble aromatic ring systems other than the diazo dye in order to obtain a general guideline for the surface-assisted photoalignment of LLC systems.

Following reports on the emergence of mesophases of aqueous solutions of sulfonated phenanthrene and naphthalene derivatives and water-soluble cyanines at an early stage of LLC researches,[12–15] systematic studies originated on LLC of aqueous solutions of an anti-asthmatic drug, disodium chromoglycate (DSCG), which possesses two chromone moieties, so that this type of LLC was called chromonic.[16] Subsequently, the characterisation and structural elucidation of the mesophases of DSCG and related compounds were achieved by some research groups.[17–23] Recently, a variety of water-soluble dye molecules such as water-soluble derivatives of xanthones,[24] cyanines,[25,26] a diazo-dye[27] and indanthrones[28] were revealed to display LLC mesophases. We selected DSCG, among the compounds reported so far for further studies on the surface-assisted photocontrol of LLC, because the drug giving LLC mesophases has been well characterised.[17–23] We report here
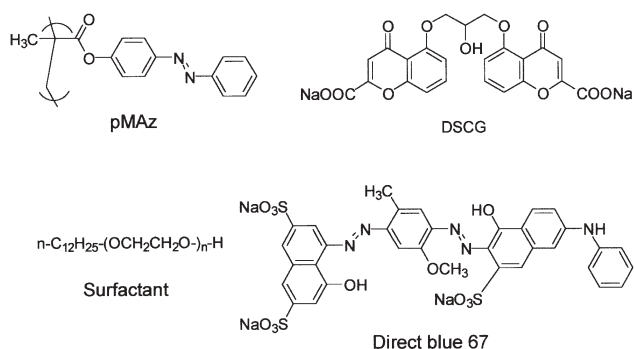
Fig. 1 Chemical structures of materials.

that LLCs derived from DSCG are effectively photoalignable by irradiation of thin films of an azobenzene polymer with linearly polarised light under critical conditions in a manner quite similar to conventional low-mass nematic TLCs.[29]

Experimentals

Materials

DSCG (Fig. 1) was kindly gifted to us by Fujisawa Pharmaceutical Co. Ltd., while poly(4-phenylazophenyl methacrylate; pMAz) (Fig. 1) was prepared according to a previous report.[30] Poly(oxyethylene) lauryl ether (Emulgen 108) as a non-ionic surfactant was purchased from Kao Co. and used as received.

Cell fabrication

Glass plates were washed successively with acetone, 6 N nitric acid, deionized water, a saturated aqueous solution of sodium bicarbonate and deionized water while undergoing ultrasonification for 15 min in each process and drying by heating. A 0.6 wt% solution in *p*-xylene of pMAz was spin-cast on cleaned glass plates to give thin films of about 7 nm in thickness. The thickness was estimated by a linear calibration line of absorbances of the azobenzene as a function of thickness. An empty cell was fabricated by setting the two plates by using film spacers of 25 μm thickness in such a way that polymer films coated on the plates are placed in a face-to-face manner. Both sides of the cell were glued with an epoxy adhesive. The cell was exposed to linearly polarised 436 nm light, followed by filling with an aqueous solution containing 11.6 wt% DSCG in the presence of a non-ionic surfactant (Fig. 1) of 0.4 wt% or 0.1 wt%, at 50 °C, by capillary action. Polarised photoirradiation with a super-high pressure mercury lamp (Ushio; UI501C) was performed by passing the light through the combination of glass filters of Y-43 and V-42 for 436 nm light and a polariser sheet. Light intensity was recorded on an optical power meter (Advantest, TQ8210).

Evaluation of photoalignment

Homogeneous photoalignment of DSCG solutions filled in cells was checked by polarised microscopic observation with a microscope (Olympus, BH-2) and evaluated by the following procedure in the same way for conventional thermotropic LC cells.[31] Linearly polarised He–Ne laser beam was passed through a cell and a crossed polariser to record transmitted light intensity as a function of rotational angle with respect to the electric vector of the actinic light. Transmittance (*T*, in %) of a cell of thickness *d* filled with LC of birefringence Δn for a probe light of wavelength λ is expressed as the following equation:

$$T = \{\sin^2(2\gamma)\,\sin^2(\pi d\Delta n/\lambda)\} \times 100 \qquad (1)$$

where γ stands for an angle contained by the director of LC and

the electric vector of the actinic light. The orientational direction of DSCG-LLC doped with a water-soluble dye, C. I. Direct blue 67, as a guest dye, was examined by monitoring the dichroism of the dye. Polarised absorption spectra of the dye-doped solutions of DSCG were recorded on a diode-array spectrometer (Hewlett-Packard, 8452A) to obtain order parameters (*S*) of both the dye and DSCG. *S* is defined as $(A_{\parallel} - A_{\perp})/(2A_{\parallel} + A_{\perp})$.[31]

Results and discussion

Photoalignment control

Previous studies on LLC using DSCG solutions revealed that the anti-asthmatic molecules are stacked in aqueous solutions to form a columnar structure, which gives rise to the generation of nematic and middle mesophases as a function of concentration.[16–23] The middle phase stems from a hexagonal packing of the columns, whereas nematic phase appears at lower concentrations as a result of the disappearance of the hexagonal packing. We have revealed, on the basis of investigation of the photoalignment control of LLC by a water-soluble dye, C. I. Direct blue 67, that nematic phase is one of the necessary conditions for the photoalignment, assisted by a photo-oriented thin film of an azobenzene polymer, pMAz4. It was confirmed that an 11.6 wt% aqueous solution of DSCG exhibiting middle mesophase displays no photoinduced alignment at all even when the solution is filled in an empty cell, surface-modified with thin pMAz films, which was exposed to linearly polarised 436 nm light in advance. Consequently, in a procedure similar to our previous work,[4] a non-ionic surfactant was added to aqueous solutions of DSCG to prepare generated nematic phase. Polarised microscope measurements confirmed that the addition of 0.4 wt% (sample A) and 0.1 wt% (sample B) of the surfactant to the DSCG solution generates nematic phase.

Photoalignment control of the LLCs was determined by filling sample-A and sample-B, respectively, into empty cells, the inside walls of which were covered with pMAz films exposed to linearly polarised 436 nm light of 1.0 J cm^{-2} in advance, followed by measuring the transmittance of a linearly polarised He–Ne laser beam as probe light as a function of rotational angles of the cells to estimate levels of photoinduced birefringence. The results are summarized in Fig. 2. In contrast to the results reported on a water-soluble dye, Direct blue 67, birefringence was induced only slightly for sample-A (open circles in Fig. 2 (a)), whereas essentially no photoalignment was generated for sample-B (open circles in Figure 2 (b)). It was found that uniaxial orientation of the mesophase is induced by heating the cells to 35 °C above the nematic–isotropic transition temperature of the solution (T_{NI}) of 28 °C for 1 min (closed circles in Figs. 2 (a) and 2 (b)). This photoalignment behaviour is quite similar to that observed for a nematic LC polymer, which is spin-cast on a film an azobenzene-containing polymer, as described in our earlier paper.[7] Wheras no uniaxial orientation of the nematic LC polymer is generated when the double-layered film was exposed to linearly polarised light at room temperature, uniform orientation is induced by heating the film at elevated temperatures above the T_{NI} of the LC polymer. The effectiveness of heating to generate the molecular orientation in LC polymers is consequently due to the marked reduction in viscosity of the LC system. This is the case also for the present LLC. No generation of photoalignment of sample-B doped with 0.1 wt% of the surfactant comes from higher viscosity, when compared with sample-B containing 0.4 wt% of the surfactant.

The photoalignment behavior of the LLC was visualised by polarised microscopic observation. As is shown in Fig. 3, sample A placed in a photoirradiated cell displays dark spots as defects with ellipsoidal shape and partial emergence of a uniaxially oriented texture even before heating. On the other
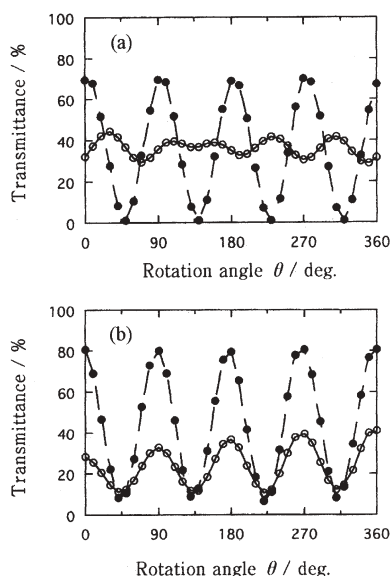
Fig. 2 Angular dependence of transmitted light intensity of linearly polarised He–Ne laser beam as a probe light passed through cells of (a) sample A and (b) sample B, respectively, before (open circles) and after (closed circles) heating at 35 °C for 1 min. The inside walls of the cells were coated with thin films of pMAz and exposed to linearly polarised 436 nm light of 1.0 J cm^{-2} before being filled with the samples.
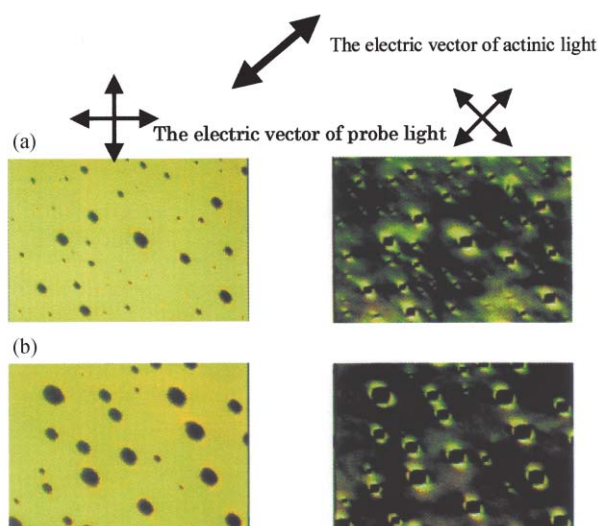
Fig. 3 Polarised micrographs of a photoaligned cell filled with sample A (a) before and (b) after annealing at 35 °C for 1 min. Two crossed thin arrows indicate the polarization plane of polarizers of the microscope, while the thick arrow corresponds to the electric vector of the actinic linearly polarised 436 nm light.

hand, sample B, exhibiting far fewer defects, shows no uniaxial orientation at all before heating, as is shown in Fig. 4, whereas a homogeneously aligned texture was obtained when the cell was heated. The results shown in Figs. 3 and 4 can be summarized as follows. First, nematic phase is a prerequisite condition for the generation of surface-assisted photoalignment of LLC in line with our previous results for the water-soluble dye.[4] Second, a lower concentration of the surfactant to induce nematic phase is preferable for the suppression of defect formation to give rise to a homogeneous texture. This situation is also in accordance with the behavior of solutions of the dye. Thirdly, in contrast to LLC of the dye solutions, heating above T_{NI} induces or enhances the photoalignment of LLC of the drug because of the higher viscosity of the latter. Fourthly, the longer axis of ellipsoidal spots as defects is in an orthogonal
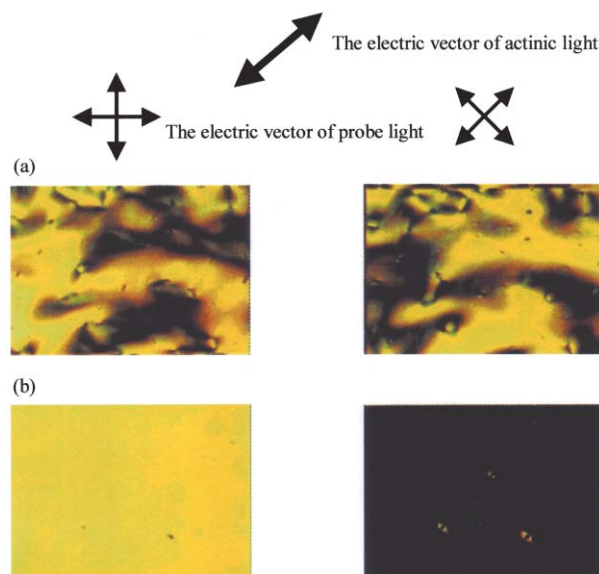

Fig. 4 Polarised micrographs of a photoaligned cell filled with sample-B (a) before and (b) after annealing at 35 °C for 1 min. Two crossed thin arrows indicate the polarization plane of polarizers of the microscope, while the thick arrow corresponds to the electric vector of the actinic linearly polarised 436 nm light.

position with respect to the electric vector of actinic linearly polarised light, implying that this kind of shape of the defects reflects the assembly of supramolecular aggregates exhibiting the columnar structuring.

In order to determine the orientational direction of DSCG molecules in the cells, the water-soluble dye (1 wt%) present as a guest was dissolved in sample -A and placed in a photoirradiated empty cell. Fig. 5 shows polarised absorption spectra of a guest–host type LLC cell, which had been exposed to linearly polarised light. There are two characteristic absorption bands due to the guest dye centered at *ca.* 550 nm and due to DSCG at shorter than 400 nm. As shown in the previous paper, the absorption band of the dye is centered at 574 nm in a dilute aqueous solution and at 522 nm in a 10 wt% solution, respectively, indicating that the absorption characteristics reflect aggregation states considerably. Consequently, the aggregation of the dye dissolved in the DSCG-LLC differs from concentrated solutions. Though absorbances of the latter are saturated, absorption bands ($A_{\parallel}$) in all wavelength regions monitored by polarised probe light parallel to the electric vector of the actinic light are larger than perpendicular absorption bands, supporting the contention that both host and guest molecules align in parallel with the electric vector of the light. Note here that the order parameter (*S*) for the dye is tiny and estimated to be 0.03, whereas the host shows $S = ca.$ 0.13, implying that dye molecules are not so homogeneously distributed in host LLC. It was described previously that $S = 0.03$ is obtained for a guest–host LLC system consisting of Congo Red as a guest dye and
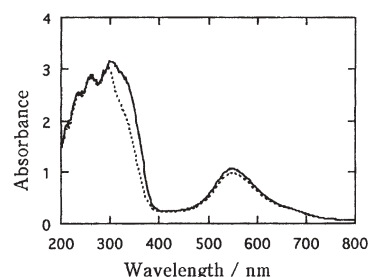
Fig. 5 Polarised absorption spectra of a cell filled with a dye-doped DSCG solution. The polarization plane of probe light is in parallel with (solid line) and perpendicular to (broken line) that of actinic light.
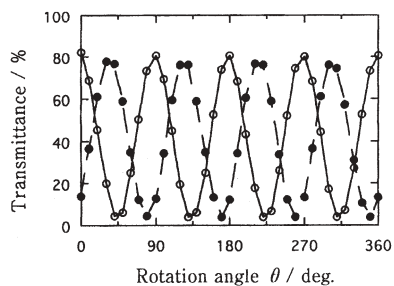
Fig. 6 Angular dependence of transmitted light intensity of linearly polarised He–Ne laser beam as a probe light passed through a photoaligned cell filled with sample A before (filled circles) and after (open circles) exposure to linearly polarised 436 nm light of 3.0 J cm^{-2} after rotating the polarization plane at 45° with respect to that of the first exposure light.
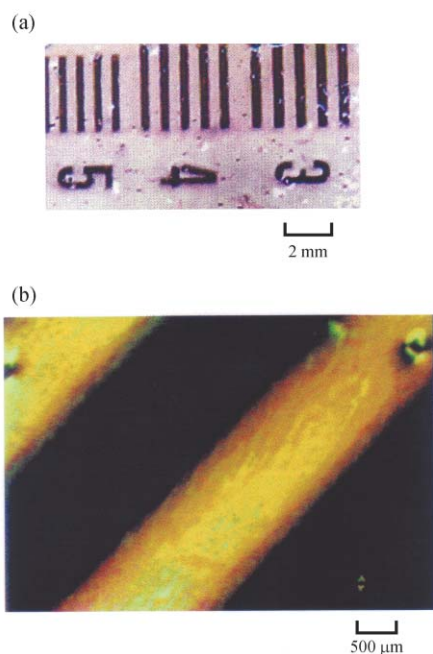
Fig. 7 Polarised micrographs of a photopatterned DSCG aqueous solution with two different magnifications.

DSCG as a host when the molecular orientation is operated by the application of a magnetic field, suggesting that both host and guest are mixed with each other less thoroughly.[32] This situation is also applicable to the present system.

Reversible photoalignment and photopatterning

It has been well established that reversible orientational control of low-mass nematic TLCs mediated by azobenzene molecules tethered to substrates' surfaces is readily operable by changing the electric vector of actinic light.[5] Similar results were observed for the LLC of DSCG, as given in Fig. 6. When a photoaligned cell was subjected to the second exposure to linearly polarised light, a 3 J cm^{-2} dose, after setting the electric vector of the light at 45° with respect to the first exposure light, the optical axis of the cell was shifted just at 45°, confirming the rewritability in LLC.

Photoimages were recorded in the LLC according to the following procedure. An empty cell coated with pMAz films was exposed to linearly polarised 436 nm light through a test chart acting as a photomask, followed by filling the cell with sample-B. Fig. 7 shows a polarised micrograph of a part of the pattern. The birefringent photoimages were recovered even after heating the cell above T_{NI}, followed by cooling down to ambient temperature. Careful microscopic observation of

bright areas of the pattern indicated that the LLC layer is comprised of assembled micro-fibrous material, which probably comes from the aggregates of columnar packing.

Conclusion

Molecules of the anti-asthmatic drug, DSCG, in aqueous solutions exhibiting chromonic mesophase are photoalignable by means of a command surface derived from thin pMAz films under irradiation with linearly polarised light. The results were all in line with those obtained for LLC of the water-soluble dye[4] as follows. First, one of the prerequisites for the photoalignment is the involvement of nematic phase, just as in the case of the water-soluble dye Direct blue 67. An efficient way to generate nematic phase of DSCG, which displays predominantly middle mesophase, is the addition of a small amount of a non-ionic surfactant. A lower concentration of the surfactant is preferable for the minimisation of defects in textures. Second, uniaxial orientation of the nematic LLC of DSCG is controllable by thin films of pMAz covering the inside walls of a cell, which has been irradiated with linearly polarised 436 nm light, followed by heating the cell at an elevated temperature above T_{NI}. This behavior differs from that of the dye LLC, which is photoalignable even at room temperature, probably because of a difference in viscosity between the two LLCs. Thirdly, the orientational direction of DSCG molecules in LLC is in parallel with the electric vector of actinic linearly polarised light for photoreorientation of the azobenzene chromophores toward the orthogonal direction. Taking notice of the fact that DSCG molecules are stacked to form columnar supramolecular aggregates leading to mesophase, the alignment of the LLC is determined by interactions between the perpendicularly oriented azobenzene with the columnar aggregates, which orient subsequently perpendicularly to the electric vector of the light. Fourthly, photoaligned textures of LLC of DSCG exhibit good thermostability and rewritability to give clear photoimages based on a difference in orientational directions of LLC.

On the basis of experimental results for both LLCs derived from DSCG and the dye described in the previous paper,[4] it is safe to conclude that the alignment photocontrol of lyotropic LCs is achievable by command surfaces when their mesophase belongs to nematic phase, just as in cases of thermotropic LCs, which have been extensively studied to find practical significances. In order to establish procedures for the photoalignment of LLCs, the optimisation of chemical structures of command surfaces and the elucidation of working mechanism for this kind of photoalignment are required, together with development of photoaligned molecular films formed by evaporation of water through nematic phases. They will appear in subsequent papers elsewhere.

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