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Surface-assisted photoalignment control of lyotropic liquid crystals. Part 1. Characterisation and photoalignment of aqueous solutions of a water-soluble dye as lyotropic liquid crystals

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The surface-mediated alignment control of a lyotropic liquid crystal (LLC) of aqueous solutions of a water-soluble dye, C. I. Direct blue 67, by using thin films of poly(4-phenylazophenyl methacrylate) as a command surface is described. Concentrated aqueous solutions of the dye in the presence of a non-ionic surfactant displayed mesophases as a chromonic LLC as a result of stacking of the aromatic ring systems leading to a columnar structure. A uniaxially oriented texture of LLC was obtained when the LLC, in the presence of a non-ionic surfactant was filled in a cell, which had been exposed in advance to linearly polarised light and was surface-modified with thin films of the polymer. The orientational direction of the dye molecules was in parallel with the electric vector of the actinic light, implying that the alignment of LLC is determined by perpendicularly photooriented azobenzene chromophores in such a way that columnar supramolecular aggregates of the dye align in parallel with the azobenzene molecular axis. Factors affecting the photoalignment control of the LLC were discussed on the basis of the results of the effects of exposure doses, excitation wavelength and photo-rewritability.

Introduction

Liquid crystals (LCs) are divided into two classes depending on whether systems contain solvents: thermotropic LCs (TLCs) and lyotropic LCs (LLCs). The former mesophases originate from their own inherent molecular skeletons, while mesophasic textures of the latter emerge in solutions of compounds, and which are not usually liquid-crystalline without solvents. In a marked contrast to versatile interest in the former from both fundamental and practical viewpoints owing to their practical applications, in particular, in display technologies, the latter has not been so far part of main stream LC research.[1,2] This is probably because of its scarce applicability to practical purposes, though the significance of lyotropic mesophases in relation to biological systems has been highly stressed.[3] By analogy to TLCs, one of the critical conditions for further advancement of LLCs is to be able to perform alignment control of the mesophases in the presence of large quantities of solvents. When compared with the alignment control of TLCs, which is a key technology for the manufacture LC display devices,[4] far less development has been achieved for that of LLCs. For instance, it was reported that LLC consisting of aqueous solutions of poly(ethylene glycol) derivatives display an uniaxially oriented texture when the LLCs are placed between a couple of silica substrates on which are deposited silver metal films, which had been rubbed prior to use.[5] Orientational control of a nematic LLC based on an aqueous solution of caesium perfluorooctanoate may be obtained to display homogeneous (uniaxially orientated) alignment when buffed substrates are employed, suggesting that the LLC alignment is induced by a topological effect of the substrate surface.[6] But no systematic study has been carried out so far on the alignment control of LLCs.

In connection with the LLC alignment, it is worth mentioning the surface-assisted orientational control of dye molecules in solutions that have been cast on substrate plates because there is the possibility that dye solutions exhibit mesophases. The first work on this subject was done by Zöcher and Coper, who observed highly uniaxially oriented molecular films of Methylene blue when an aqueous solution of the blue dyestuff was coated on a rubbed silica plate.[7] Structural analysis was later performed by Anderson to reveal that dye molecules align in the film in such a way that the long molecular axis orients perpendicularly to the rubbing direction.[8] This technique was applied by Sato and co-workers to produce a circular polariser comprised of orientationally controlled microcrystals of the water-soluble dye.[9] It was Dryer and Ertel who developed anisotropic dye films applicable to polarisers by spreading aqueous solutions of various kinds of dyes on rubbed substrate plates not only of silica glass, but also of metals and plastics.[10a,b] It was observed by West that an aqueous solution of a dye exhibits a schlieren texture characteristic to that of nematic phases on a non-rubbed substrate surface.[10c]

We have previously focused our attention on the scope and limitation of the functions of command surfaces[11] that demonstrate surface-assisted photoalignment control of LC systems including low mass nematics,[12] polymeric nematics,[13] discotic nematics[14] and chiral nematics,[15] all of which belong to the TLC class. Command surfaces are composed of molecular as well as polymeric ultra-thin films incorporating photoreactive moieties tethered to the uppermost substrate surfaces to be subjected to photoinduced control of molecular orientations, which are transferred to LC layers to give rise to aligned LC textures.[11] During the course of our studies on molecular photoalignment control we observed that uniaxially oriented

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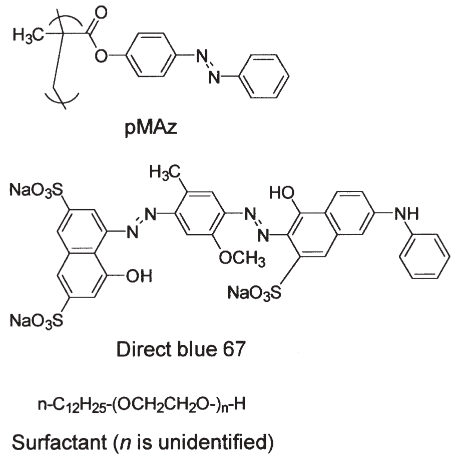

Fig. 1 Chemical structures of the materials.

dye molecular films are formed by spin-coating of an aqueous solution of a water-soluble bis-azo dye, C. I. Direct blue 67 (Fig. 1), onto a film of a polymer with azobenzene side chains, which has been exposed to linearly polarised light in advance.[16] We suggested subsequently that a lyotropic mesophase of the dye solution plays an essential role in photoalignment to give anisotropically oriented dye molecular films[17] which possess microfibrous morphologies due to supramolecular aggregates of the dye molecules.[18] We report here the characterisation of aqueous solutions exhibiting lyotropic mesophases and photoalignment control of the aqueous solutions of the dye using thin films of an azobenzene polymer to give anisotropic photoimages exhibiting excellent thermostability below the transition temperatures between the nematic and isotropic phases of the LLC. This is the first example of orientational photocontrol of LLC,[19] whereas the surface-assisted photocontrol of thermotropic LCs has been extensively investigated.[11,20]

Experimental

Materials

The water-soluble dye, direct blue 67, was a gift from Nippon Kayaku Co. Ltd. and used as received. Poly(4-phenylazophenyl methacrylate) (pMAz in Fig. 1) was prepared according to our previous paper.[21] Poly(oxyethylene) lauryl ether (Emulgen 108), as a non-ionic surfactant, was purchased from Kao Co. and used as received.

Sample preparation

Glass plates were washed successively with acetone, 6 M nitric acid, deionized water, a saturated aqueous solution of sodium bicarbonate and deionized water under application of ultrasonification for 15 min for each process and dried by heating to give plates with contact angles of less than 10° for water. 0.6 wt% of pMAz in *p*-xylene was spin-cast on cleaned glass plates to give thin films of about 7 nm thickness. The thickness was estimated from a linear calibration line of the absorbance of the azobenzene as a function of thickness. An empty cell was fabricated by separating two plates using film spacers of 25 μm thickness in such a way that polymer films coated on the plates are placed face-to-face and filled with a dye solution at 50 °C by capillary action. Both sides of the cell were glued with an epoxy adhesive. Polarised photoirradiation with a super-high pressure Mercury lamp (Ushio, UI501C) was performed by passing the light through a combination of UV-35 and UV-D35 (Toshiba Glass) glass filters for 365 nm light and through Y-43 and V-42 filters for 436 nm light and also a polarizer sheet. The light intensity was recorded on an optical power meter (Advantest, TQ8210).

Physical measurements

Electronic absorption spectra were recorded on a diode array spectrometer (Hewlett Packard, 8452A), while a microspectrometer (Hitachi, U-6500) was used for absorption spectra measurements of LLC cells with a beam spot of 1 μm diameter. Polarised microscopic observations were carried out using a microscope (Olympus, BH-2). Temperatures of cells were controlled using a hot plate (Mettler, FP80) for both absorption spectra measurements and microscopic observation. X-Ray diffraction analysis was conducted on a Rigaku-Denki RU-200 after a sample solution in a sealed capillary of a 1.5 mm diameter was subjected to a magnetic field application at 5 T at 50 °C, followed by gradual cooling down to an ambient temperature.

Results and discussion

Liquid crystallinity of dye solutions

A droplet of a 5wt% aqueous solution of the dye containing 0.5 wt% of a non-ionic surfactant (Fig. 1) was placed between two glass plates, fabricating an open cell with a cell gap of 10 μm, and examined by polarised microscopy. Whereas the whole area of the fluid film was quite dark, we observed that the periphery of the solution became bright when left to stand at ambient temperature, as shown in Fig. 2(a), suggesting that a lyotropic mesophase emerges at the peripheral regions as a result of the evaporation of water where the local concentration of the dye is enhanced. Encouraged by these results, polarised microscope observations were made of sealed cells of solutions of the dye at various concentrations in the absence and in the presence of a non-ionic surfactant. As shown in Fig. 2(b), a 10 wt% solution with 0.5 wt% of the surfactant displays schlieren texture, indicating that the solution is nematic at room temperature. The texture of a solution in the absence of the surfactant was quite different from that in the presence of the surfactant and is not nematic, as presented in Fig. 2(c). The texture was also critically dependent on the concentration of the dye, as seen in Fig. 2(d), which shows a polarised micrograph of an 8 wt% solution of the dye in absence of the surfactant.

There are literature reports suggesting that some dye solutions exhibit mesophases,[22,23] and a pioneering study on LLCs of water-soluble diazo-dyes was carried out by Lydon.[24]

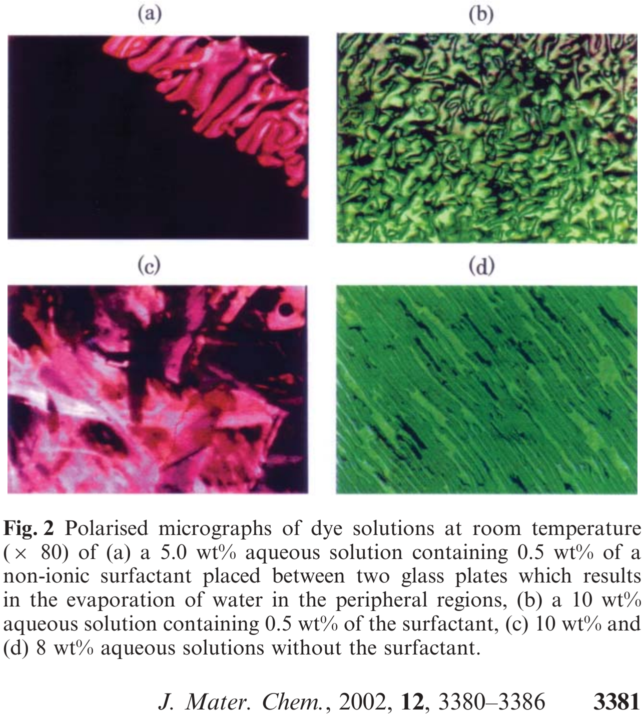

Fig. 2 Polarised micrographs of dye solutions at room temperature (× 80) of (a) a 5.0 wt% aqueous solution containing 0.5 wt% of a non-ionic surfactant placed between two glass plates which results in the evaporation of water in the peripheral regions, (b) a 10 wt% aqueous solution containing 0.5 wt% of the surfactant, (c) 10 wt% and (d) 8 wt% aqueous solutions without the surfactant.

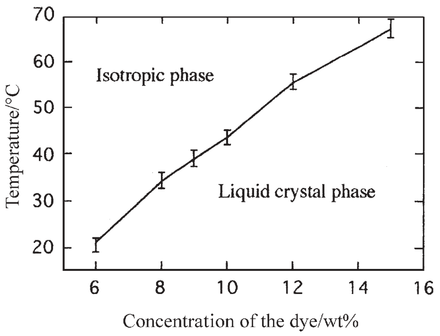

Fig. 3 Phase diagram of the dye–water system.

Recent work has revealed that aqueous solutions of other dyes such as derivatives of xanthone,[25] cyanine,[26] indanthrone[27] and benzopuprin 4B,[28] are lyotropic. Consequently, Direct blue 67 belongs to this family of so-called chromonic LLCs.

Heating of the cells exhibiting lyotropic mesophases resulted in the sudden disappearance of optical anisotropy due to transition to the isotropic phase. No schlieren texture was observed during the heating for any of the solutions containing no surfactant, indicating that the lyotropic nematic phase arises from the presence of the surfactant. The mesophases of all of the cells were recovered upon cooling. Consequently, the transition temperatures of the solutions were estimated by polarised microscopy observation. Fig. 3 shows transition temperatures as a function of dye concentrations in the absence of the surfactant. The higher the concentration, the higher the transition temperature.

Electronic absorption spectra of the solutions were recorded by placing them between a couple of glass plates, pressing them to adjust the thickness of the thin liquid film and sealed. The absorption maximum ($\lambda_{\max}$) of a dilute solution of the dye was centered at 574 nm, whereas $\lambda_{\max}$ of a 10 wt% solution appeared at 522 nm, indicating strong H-aggregation of the dye in concentrated solutions. Fig. 4 shows the absorption spectra of an 8 wt% solution at room temperature and at a higher temperature. A slight red shift of 2 nm was induced by the transition from the lyotropic to the anisotropic phase, implying that the nature of the H-aggregates in the dye is relatively less temperature-dependent. The absorbance of the dye increased markedly after the transition to the isotropic phase. There are two possible explanations for a phase transition to cause such a change in absorbance . The first one is that the level of H-aggregation is temperature-dependent, whereas the second one is based on changes in molecular orientation of the H-aggregates below and above the transition temperature.

In order to obtain further information about the molecular arrangements of the dye in aqueous solutions, wide angle X-ray diffraction analysis was achieved for 10 wt% of dye solutions in the absence and in the presence of 1 wt% of the surfactant. Samples in sealed capillary tubes were exposed to a strong magnetic field during the gradual lowering of temperature from an isotropic to an ambient temperature in order to induce molecular orientations. A reflection band was observed in the diffraction patterns recorded at an ambient temperature for the dye solutions in the direction perpendicular to that of the applied magnetic field, irrespective of the presence of the surfactant, being equivalent to a 0.34 nm spacing. These results imply that the spacing arises from the periodical stacking of the aromatic ring systems, which are packed in a direction perpendicular to the applied magnetic field direction for both lyotropic mesophases to form supramolecular columns. On the other hand, small angle X-ray diffraction patterns of the dye solutions were influenced critically by the presence of the surfactant. Whereas no small angle diffraction was observed for the sample in the presence of the surfactant, a reflection emerged for the dye solution in the absence of surfactant in the direction perpendicular to the applied magnetic field, indicating that the corresponding spacing is 5.7 nm. The sample without the surfactant forms a highly ordered supramolecular structure exhibiting packing of supramolecular columns to give rise to a mesophase other than a nematic one, as illustrated in Fig. 5 for the proposed model, in a manner similar to other LLCs previously reported in the literature.[29,30] On the other hand, addition of the surfactant modifies the mesophase to give nematic mesophase, as supported by the polarised microscopic observation.

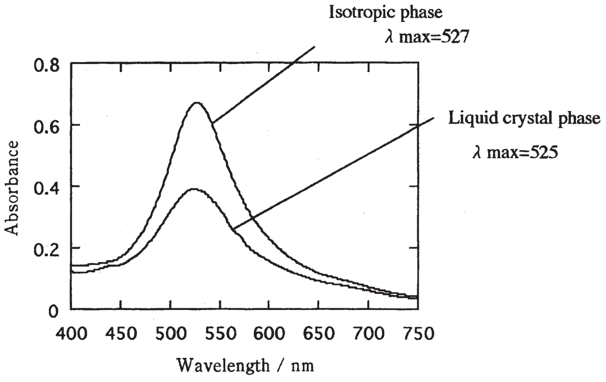

Fig. 4 Absorption spectra of a 8n wt% aqueous solution of the dye in (a) the liquid crystal and (b) isotropic phases.

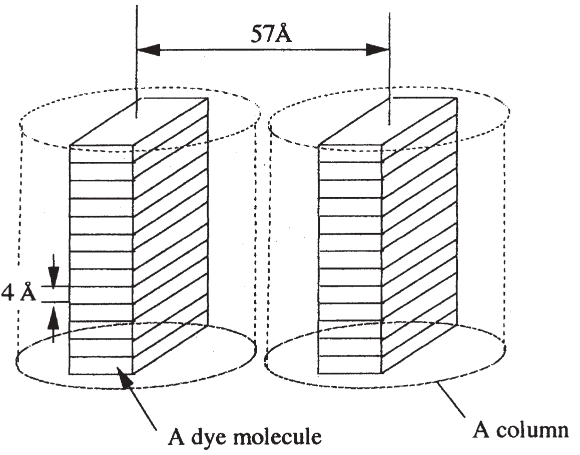

Fig. 5 A model for the supramolecular structure of the dye in a mesophase.

Photoalignment of the lyotropic mesophase

It is well established that irradiation of thin films of polymers with azobenzene side chains with linearly polarised light gives rise to molecular reorientation of the chromophore to form optically anisotropic films as a result of the repetition of *E–Z* photoisomerisation and that the photogenerated molecular orientation of the azobenzene is efficiently transferred to nematic TLCs.[11] Accordingly, we attempted to achieve the photoalignment of nematic LLCs of the dye solution containing the surfactant. Three kinds of dye solutions were prepared, as listed in Table 1. An empty cell surface-modified with pMAz

Table 1 Concentrations of aqueous solutions of the dye

	Conc. (wt%)	
Sample No.	Dye	Surfactant
1	10	1.0
2	9	0.4
3	9	0.2

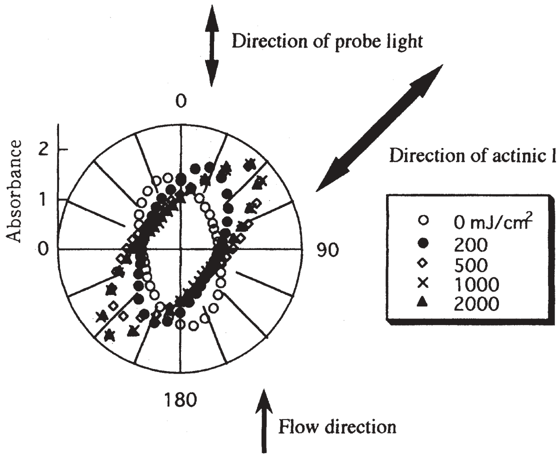

Fig. 6 Circular diagrams of polarised absorbances of No. 1 (open circles), No. 2 (triangles) and No. 3 (crossed squares) at 633 nm. Cells modified with thin films of pMAz, which had been exposed to linearly polarised 436 nm light of a 1 J cm^{-2} dose in advance were filled with the solutions listed in Table 1.

films was exposed to linearly polarised 436 nm light to generate a photo-oriented state and subsequently filled with each dye solution. The orientational directions of dye molecules were evaluated by passing a linearly polarised He–Ne laser beam at 633 nm through the cells, whereas the red light is absorbed so weakly, as shown in Fig. 4, that the absorption of the probe light is not saturated. The results summarized in Fig. 6 tell us the following. First, the transition moments of the dye molecules are in parallel with the electric vector of the actinic light for all of the samples, whereas the dichroic ratios depend on the formulation. Second, the orientation of the dye molecules is not affected at all by the flow direction of the sample solutions, indicating that the dye orientation stems specifically from the photo-oriented polymer film.

Fig. 7 shows micrographs of the cells observed by linearly polarised probe light. In accordance with the results shown in Fig. 6, the transition moment of the dye is precisely in parallel with the electric vector of the actinic light. Fig. 7 also indicates that the liquid films contain many black spots with ellipsoidal shapes as defects, while sample No 3 with the lowest concentration of surfactant contains the smallest number of defects. Note here that no photoalignment was generated when a dye solution without the surfactant was used, showing that the nematic phase is a necessary condition for the photoalignment control of LLC. In order to shed light on the nature of the defects, polarised absorption spectra of μm regions of inside and outside of the defects were performed. Because the cell of 25 μm thickness is not suitable for absorption measurements, the cell thickness was much reduced by strongly pressing the substrate plates. As shown in Fig. 8, the inside of a black defect has strong absorbances, irrespective of the electric vector of probe light, whereas the outside of the defect is highly dichroic. In other words, the ellipsoidal defects are comprised of the isotropic phase of a dye solution and very likely originates from the local concentration of the surfactant. This assumption is in line with the fact that a decrease in surfactant concentration is effective for the suppression of defect formation.

The alignment control of lyotropic LC systems assisted by substrate surfaces has been scarcely understood.[4] In order to obtain some insight into the mechanism of the photocontrol of the lyotropic LCs, the evaluation of a photoalignment of polymer films was carried out. Linearly polarised light irradiation of a thin film of the polymer with azobenzene side chains (pMAz) results in the dichroism of azobenzene chromophores with a relatively small dichroism (= 0.08). This means that the orienational control of the lyotropic LCs stems specifically from photoaligned azobenzene units. This situation leads to the assumption that the orientation of lyotropic LCs arises from interactions of surface azobenzenes with supramolecular aggregrates of dye molecules.

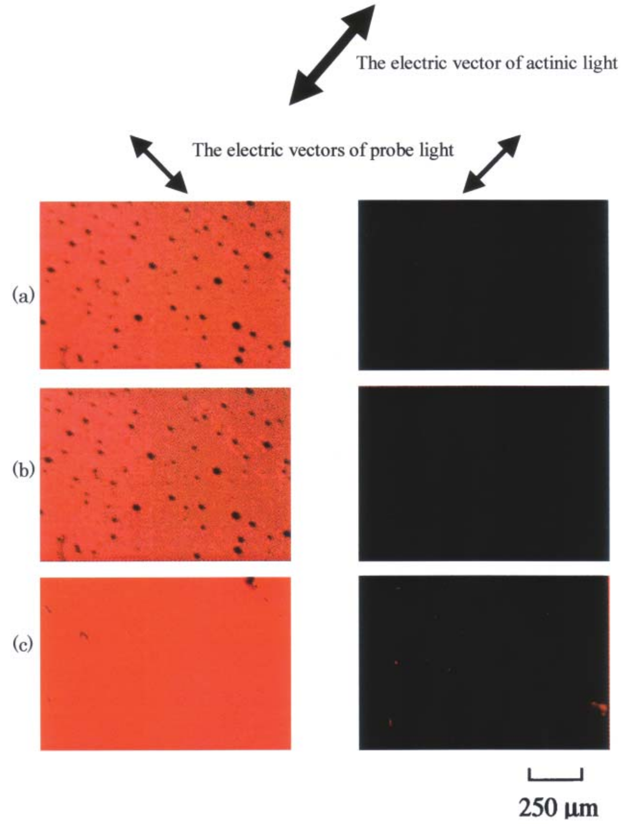

Fig. 7 Polarised micrographs of (a) No. 1, (b) No. 2 and (c) No. 3 (Table 1) in cells modified with thin films of pMAz, which had been exposed to linearly polarised 436 nm light of a 1 J cm^{-2} dose in advance. The arrows show the directions of electric vectors of actinic light (broad line) and probe light (thin lines).

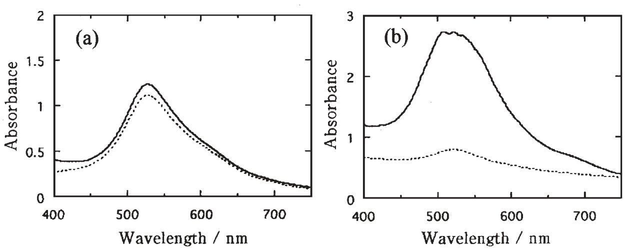

Fig. 8 Polarised microscopic absorption spectra of (a) the inside and (b) the outside of a black spot observed in the polarised micrograph of No. 2 shown in Fig. 7(b). The diameter of the perpendicular (full lines) and parallel (dashed lines) polarised probe light beam was 1 μm.

Based on these results, photoimage formation of LLCs was carried out by imagewise exposure of an empty cell. The cell was exposed to a flood of linearly polarised light in advance, followed by irradiation with light through a photomask after rotating the electric vector at 90° to generate latent photoimages in azobenzene polymer films. As presented in Fig. 9, images based on the difference in the molecular orientation of dye molecules were obtained. These were quite stable toward heat and light even though the LLC contains 90 wt% of water.

Factors affecting the photoalignment

Exposure doses. In order to estimate a minimum exposure dose of linearly polarised 436 nm light required for the

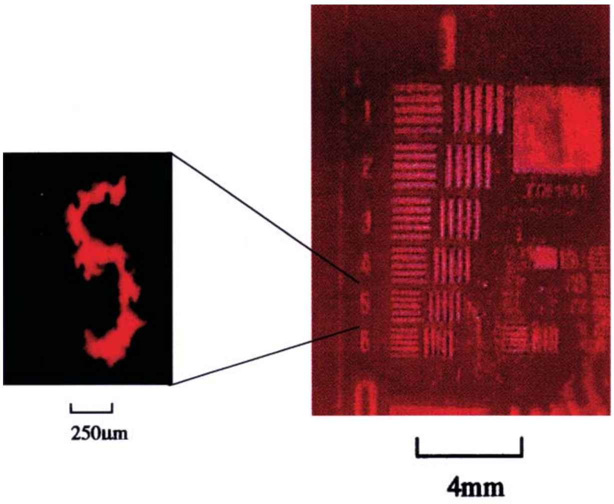

Fig. 9 Polarised micrographs of a test chart (right hand panel) and of an enlarged image recorded in a dye solution (No. 3 in Table 1).

photoalignment of the LLCs of dye solutions, empty cells were exposed with light of various doses, and then filled with a 9 wt% dye solution containing 0.2 wt% of the surfactant (sample No. 3) by capillary action. As shown in Fig. 10, a flow-assisted orientation was observed for a non-irradiated cell. Levels of orientation of dye molecules induced by photoirradiated polymer films were saturated at an exposure dose of about 500 mJ cm^{-2}, at which dose the order parameter of the azobenzene in a film of the polymer levels off. Note that the photoalignment control of low-mass nematic LCs mediated by films of azobenzene polymers is in general conducted under exposure conditions of a few 10 mJ cm^{-2} doses or less. An exposure dose one order magnitude larger is required for the photoalignment of LLC, implying that the photoalignment mechanism for LLC is somewhat different from TLC. It is readily assumed that it is very difficult for each dye molecule in mesophases to interact directly with photo-oriented azobenzene units of a film because the liquid crystallinity comes from the stacking of dye molecules to form supramolecular columnar structures with gigantic sizes when compared with low mass TLC molecules, which are of shapes and sizes similar to the azobenzene moiety. In other words, the lower exposure doses required for photoalignment is due to the effective cooperativity between low mass TLC molecules owing to their relative molecular mobility, when compared with gigantic supramolecular aggregates.

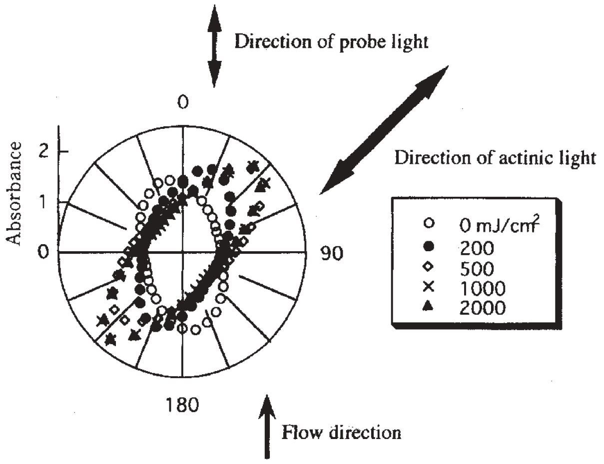

Fig. 10 Circular diagrams of polarised absorbances of No. 3 in Table 1 at 633 nm as a function of exposure doses. The solutions of No. 3 were in cells modified with thin films of pMAz, which had been exposed to linearly polarised 436 nm light of 0.0 J cm^{-2} (open circles), 0.2 J cm^{-2} (closed circles), 0.5 J cm^{-2} (open diamonds), 1.0 J cm^{-2} (crosses) and 2.0 J cm^{-} (closed triangles) doses in advance, respectively.

Excitation wavelength. Photoreorientation of azobenzene side chains tethered to polymer backbones has been conducted usually by using linearly polarised 436 nm light, which leads to preferential formation of rod-shaped, thermodynamically more stable *E*-isomer in the photostationary state. It is an interesting subject whether linearly polarised 365 nm light can also induce the photoalignment of LC systems as a result of the photoreorientation of azobenzene chromophores, because UV irradiation results in the *Z*-isomer with a bent form as the predominant component in the photostationary state. In this context, an empty cell was exposed to linearly polarised 365 nm light to determine whether the light causes uniaxial alignment of the LLC of a dye solution. The result given in Fig. 11 reveals that the parallel photoalignment of the dye in the LLC is also generated by 365 nm irradiation so that the photoalignment is insensitive to the wavelength of the actinic light.

An LLC cell photoaligned by irradiation with linearly polarised 365 nm light was heated at 60 °C, at which temperature the LLC became isotropic, to determine the thermostability of the photoalignment. It was found that the axial orientation of the dye molecules is maintained even after heating for 2 h though the dichroic ratio is reduced about by half.

Reversiblity of the photoalignment. Orientational directions of photogenerated homogeneous alignment of TLCs is readily manipulated by changing the directions of the electric vector of the actinic light when azobenzene chromophores are incorporated in the command surfaces, because of their reversible photoisomerizability with excellent photofatigue-resistance.[4] The reversibility of photoalignment of the LLCs of an 8 wt% dye solution was examined by the following procedure. A cell filled with photo-oriented LLC, which was prepared as stated above, was subjected to exposure to linearly polarised 436 nm light, the electric vector of which was set at 45° with respect to that of the first exposure. When the cell was subjected to the photoirradiation at an ambient temperature, no orientational modification was induced even after an exposure of a 10 J cm^{-2} dose. On the other hand, as shown in Fig. 12, the reorientation of dye molecules took place upon exposure of doses of more than about 3 J cm^{-2} when both substrate plates were irradiated at 50 °C, where the solution exhibited the isotropic phase. It should be noted here, however, that the reoriented direction of the dye is perpendicular to the electric vector of the second

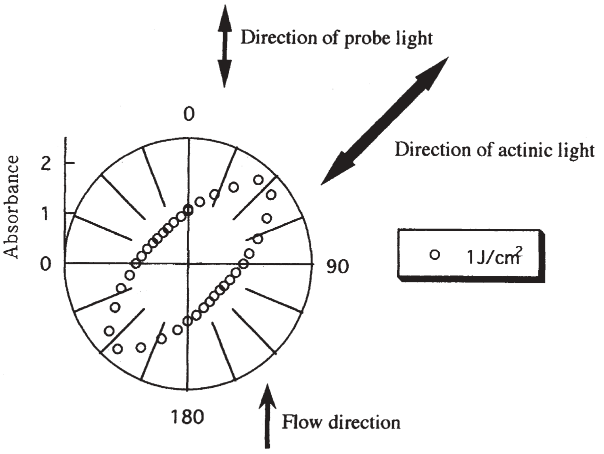

Fig. 11 Circular diagrams of polarised absorbances of No. 3 in Table 1 at 633 nm. No. 3 was filled in a cell modified with thin films of pMAz, which had been exposed to linearly polarised 365 nm light of 1.0 J cm^{-2} in advance.

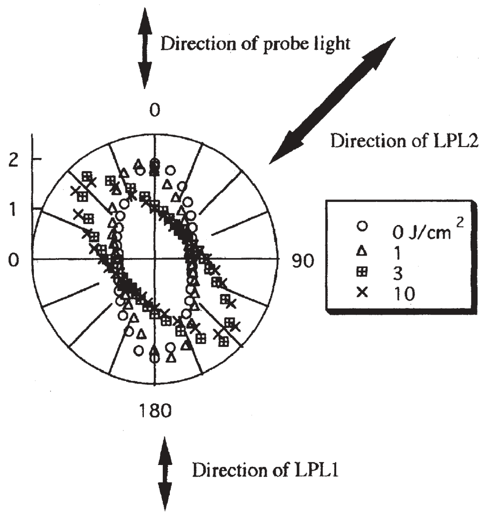

Fig. 12 Circular diagrams of polarised absorbances at 633 nm of a photo-reoriented cell filled with No. 3. The cell modified with pMAz films was irradiated with linearly polarised 436 nm light in advance, followed by exposure to the same light of 0.0 J cm^{-2} (open circles), 1.0 J cm^{-2} (open triangles), 3.0 J cm^{-2} (open crossed squares) and 10 J cm^{-2} (crosses) after setting the electric vector at 45° in respect with that the initial exposure.

actinic light, in sharp contrast to the fact that the first irradiation had resulted in a parallel orientation, as shown above. Though further study is needed, it is assumed that the surface-assisted reorientation of dye molecules comes from direct interactions of dye molecules with photo-oriented azobenzene moieties as a consequence of partial dissociation of supramolecular aggregates of the dye molecules at the elevated temperature to give the isotropic phase. This situation is similar to cases of conventional low-mass nematic LCs. Note here that, as discussed above, parallel orientation of LLCs may stem from interactions of supramolecular aggregates giving a columnar structure.

Conclusions

The following conclusions regarding the photoalignment control of dye LLCs can be drawn from the results mentioned above. First, the generation of a lyotropic mesophase of a water-soluble dye in aqueous solutions stems from supramolecular aggregates, which are formed as columnar structuring of stacked dye molecules, as shown in Fig. 5. Second, the addition of a surfactant is a critical condition for generating the nematic phase of the lyotropic mesophase of aqueous solutions of the water-soluble dye, and the nematic phase is specifically photoalignable. Thirdly, the minimization of surfactant concentration plays a significant role in suppressing the formation of defects, which are due to an anisotropic phase. Fourthly, the orientational direction of transition moments, which are likely in accordance with the longer molecular axis of the dye, is in parallel with the electric vector of the actinic linearly polarised light when an empty cell irradiated with linearly polarised light for before filling with the LLC solution. The columnar structures align perpendicular to the electric vector of the actinic light, since the molecular axis of the dye aligns in the orthogonal position with respect to the orientational direction of columns consisting of stacked dye molecules. Fifthly, the reorientation of the LLC can be achieved by irradiation of a homogeneously photoaligned cell with linearly polarised light at an elevated temperature to give the isotropic phase, whereas the orientational direction of dye molecules is perpendicular to the electric vector of the light, in contrast with the parallel photoalignment of the dye which is obtained when polarised irradiation is performed on an empty cell. The contrasting results may arise from differences in the interactions of dye species with photo-oriented azobenzene units at the uppermost cell surfaces; whereas interactions of supramolecular aggregates of the dye exhibiting columnar structuring in the lyotropic nematic phase with azobenzene units gives rise to parallel photoalignment of dye molecules, perpendicular photoalignment comes from direct interactions of dissociated dye molecules with the azobenzene in the isotropic phase. Finally, the photoaligned LLCs of the dye are stable toward heat and light so that stable photoimages were obtained, even though the system contains 90 wt% of water or more, as a result of the transfer of latent images formed by linearly polarised light irradiation of azobenzene polymer films to an LLC layer.

The present study reveals that surface-assisted photoalignment by using command surfaces is achieved even for supramolecular aggregates, which are the origin of the lyotropic mesophase, probably as a result of interactions of photo-oriented azobenzene units of nm size with aggregates of much larger sizes. In this respect, further investigation is needed for the elucidation of the photoalignment mechanism of LLCs. This is not only because sizes and shapes of interactive species at the interface between an LLC layer and a polymer surface are quite different, but also because columns comprised of stacked dye molecules are likely covered with highly hydrophilic sulfonate residues so that direct interactions of the aggregates with relatively hydrophobic azobenzene units seem to be less effective. On the other hand, from a practical viewpoint, the alignment photocontrol of LLCs is of great significance, since oriented dye molecular films are readily fabricated by the evaporation of water from LLCs[16–19] and are applicable to micro-patterned polarizing elements for stereoscopic liquid crystal displays.[31] Detailed results of the photoalignment of dye molecular films through the lyotropic phase will be presented elsewhere.

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