Photoimages Formed by Lyotropic Liquid Crystals

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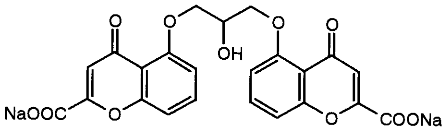
The orientation of lyotropic liquid crystals consisting of about 90 wt% water is controllable on thin films of a polymer with azobenzene side chains, which are exposed to linearly polarized light, to give rise to thermally stable birefringent photoimages.

Liquid crystals (LCs) are devided into two classes; thermotropic and lyotropic ones.[1–3] The former mesophases originate from their own inherent molecular skeletons, while mesophasic textures of the latter emerge in solutions of compounds which are usually not liquid crystalline without solvents. In a marked contrast to versatile interest in the former from both fundamental and practical viewpoints owing to the applications, in particular, to display technologies, the latter has been so far out of the main stream of LC researches. During the course of our systematic studies on the alignment manipulation of LCs by command surfaces fabricated by photoactive molecular as well as polymeric films,[4] we reported previously that uniaxially oriented dye molecular films are formed by spin-coating of an aqueous solution of a water-soluble dye on a film of a polymer with azobenzene side chains, which is exposed to linearly polarized light in advance.[5] We suggested that a lyotropic mesophase of the dye solution plays an essential role in the photoalignment to give the photooriented dye films,[7] which display fibrous textures in their morphology due to supramolecular aggregates of the dye molecules.[6] This report deals with the unquivocal observation that aqueous solutions exhibiting a lyotropic mesophase gives thermally stable photoimages on a photoaligned polymer even though the systems contain a large amount of water. This is the first example of the orientational control of lyotropic LCs, whereas the surface-assisted photocontrol of thermotropic LCs has been extensively investigated.[8]

Lyotropic LCs are classified into three sub-groups on the basis of the nature of component molecules; amphiphilic, polymeric and chromonic lyotropic LCs.[9] The chromonic lyotropic LCs are formed in highly concentrated aqueous solutions of some of water-soluble disk-shaped polyaromatic molecules with hydrophilic substituents.[10] We selected a family of anti-asthmatic drugs, which possess common chemical structures of polyaromatic rings with carboxylate groups, display mesophasic textures when they are dissolved in water in high concentrations.[11]

Photoalignment experiments were performed according to our conventional procedure for the photocontrol of thermotropic nematic LCs.[4] An empty cell was fabricated by using a couple of substrate glass plates, the inside walls of which were covered with thin films of a photo-reactive polymer, poly(4-methacryloylazobenzene); (pMAz). The cell was exposed to linearly polarized 436 nm light, followed by being filled with an aqueous solution of disodium chromoglycate (DSCG),[11] a representative anti-asthmatic drug, containing a small amount of a non-ionic surfactant. It was found that a uniaxial orientation of the lyotropic LC is in fact generated to give a birefringence solution and that the orientational direction of the mesophase is governed by the electric vector of the actinic light. This allowed us to record photoimages in an aqueous solution of the drug. As shown in Figure 1, photoimages are visualized by placing a cell between a couple of crossed polarizers owing to the photogenerated birefringence. The images are quite stable at an ambient temperature even though the LC consists of about 90 wt% of water.



DSCG

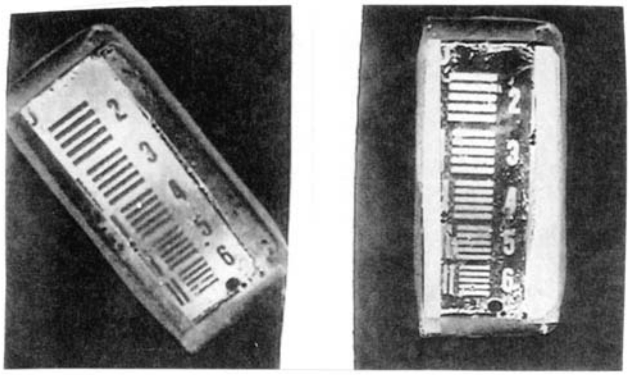


Figure 1. Photographs of a cell (1 × 3 cm^2) filled with a 10 wt% aqueous solution of DSCG containing 1 wt% of a non-ionic surfactant. An empty cell was fabricated with two glass plates spin-cast with pMAz thin films using a film spacer of 25 μm thickness and exposed to linearly polarized 436 nm light of 1 J cm^{-2}, followed by the second exposure to the same light through a photomask after rotating the electric vector of the actinic light. A 11.6 wt% aqueous solution of DSCG containing 0.4 wt% of a non-ionic surfactant was filled in the cell at 50 °C and kept standing for 1 min at 35 °C to be subjected to photoimage observation at room temperature by placing the cell between two polarizers in a crossed position.

Encouraged by these results, the command-surface-assisted photoalignment technique was applied to a concentrated aqueous solution of the water-soluble bisazo-dye, C. I. Direct Blue 67 (Figure 2), which forms a uniaxially aligned dye molecular film on a photoaligned pMAz simply by spin-coating and drying.[5–7] It was found that a 10 wt% aqueous solution of the dye shows a typical Schlieren texture, exhibiting a lyotropic nemat-

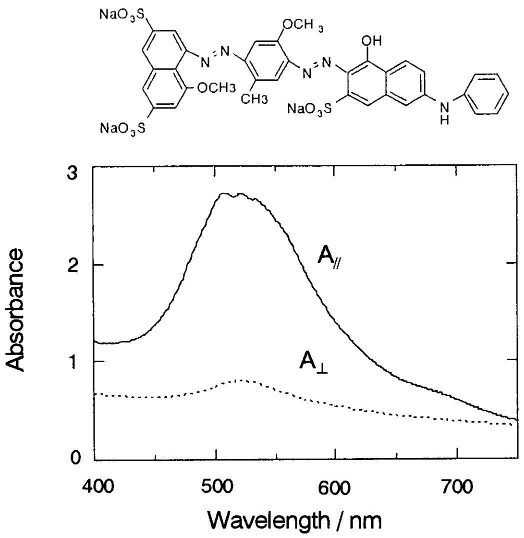


Figure 2. Polarized absorption spectra of a 10 wt% aqueous solution of C. I. Direct Blue 67 filled in an empty cell, the inside walls of which were spin-coated with pMAz films and exposed to linearly polarized 436 nm. $A_{//}$ and $A_{\perp}$ denote absorption spectra taken by probe light with the electric vectors parallel and perpendicular to that of the actinic light, respectively.

ic LC phase which possesses a nematic/isotropic phase change temperature (T_{NI}) at 46–49 °C. X-ray diffraction analysis suggested that dye molecules in the mesophase are stacked with a 0.34 nm spacing to form a columnar structure whereas the distance between columns was estimated to be 5.7 nm. Homogeneous alignment of this lyotropic LC was generated in the same manner as described above by filling the aqueous solution of the dye in an empty cell, which was modified with thin films of pMAz and irradiated with linearly polarized light in advance. Figure 2 shows polarized visible absorption spectra of the photo-oriented solution in the cell, indicating that dye molecules align in parallel with the electric vector of the actinic light for the azobenzene photochemistry. The surface-assisted dichroism of the dye solution disappeared completely above T_{NI} and was regenerated without marked deterioration upon cooling down below T_{NI}. Furthermore, it was found that the orientational direction of the dye is controllable by irradiation of the cell filled with the dye solution with linearly polarized light to display rewritability.

The alignment control of lyotropic LC systems assisted by surfaces has been scarcely understood.[12] 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. A thin pMAz film exposed to the polarized light exhibited a relatively small dichroic ratio (= 0.08) on the basis of polarized UV–visible absorption spectra. Polarized FT-IR spectra showed that the ester C=O groups showed a photoinduced reorientation with a much smaller dichroic ratio (= 0.008) so that the orienational control of the lyotropic LCs stems specifically from photoaligned azobenzene units. But it is hard to imagine that water-soluble molecules interact directly with relatively hydrophobic photoaligned azobenzene residues at the interface between a mesophasic aqueous layer and a polymer film surface. In other words, the orientation of lyotropic LCs arises not from direct molecule-to-molecule interactions between the water-soluble molecules and the photoaligned azobenzene residues. At the present, we have no reasonable interpretation of the orientational photocontrol of the lyotropic LCs, because the dimension is quite different between the azobenzene in a nm level and supramolecular aggregates of component molecules giving rise to lyotropic mesophases, which consist of supramolecular aggregates rather in a macroscopic level.[6]

In summary, the first observation has been made on the alignment photocontrol of a lyotropic mesophase assisted by a photo-oriented molecular thin films of a photo-reactive polymer. This may lead to practical applications of unexplored lyotropic LCs, since optically oriented molecular films are fabricated by casting mesophasic aqueous solutions on photoaligned films and subsequent drying.

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