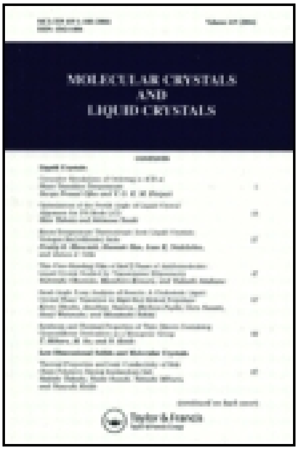

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PHOTOREGULATION OF LIQUID CRYSTAL ALIGNMENT INDUCED BY POLARIZATION PHOTOCHROMISM OF MOLECULAR FILMS

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Abstract A photochemical way to regulate azimuthal alignment of nematic liquid crystals is presented. Surface of a silica substrate plates was modified with photochromic units to fabricate a liquid crystal cell with use of the plate. Exposure of the cell to linearly polarized light for the photochromic reactions induced homogeneous alignment.

INTRODUCTION

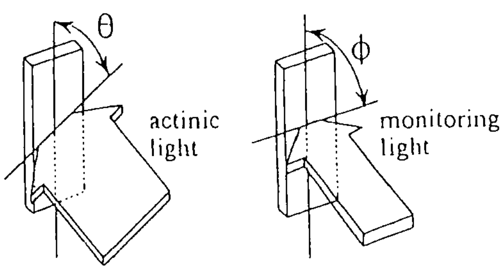
Photochemical switching of liquid crystals induced by photochromic molecules has been attracting current interest in relation to the potential applicability to optical memory, display devices as well as light modulators. According to our works, surface modification of substrate plates with photochromic moieties including azobenzenes brings about reversible alignment alteration of nematic liquid crystals upon alternate exposure to light for the surface photochromism.[1] We proposed to call such surfaces "command surfaces" since the reorientation of a large number (ca. 10^4) of liquid crystal molecules is induced by a single photochromic molecule.[2]

When actinic light is linearly polarized, different events occur. Irradiation with linearly polarized UV light for the isomerization from the trans to the cis isomer causes the formation of uniaxial in-plane (homogeneous) alignment.[3] Closely related works on surface-assisted uniaxial alignment of liquid crystals have been recently reported with use of polymer thin films doped with dichroic dyes.[4,5] This paper concerns to review our recent studies on novel photon-mode liquid crystal cells displaying azimuthal reorientation of liquid crystals driven by linearly polarized light.

SURFACE TREATMENT AND CELL FABRICATION

Surface of a quartz plate was treated with a silylating reagent bearing a photochromic unit to fabricate a hybrid-type cell by sandwiching a nematic liquid crystal, (EXP-CIL of T_{NI}=30.6℃ or DON-103 of T_{NI}=74℃ of Rodic), between the plate and a quartz plate which is surface-modified with lecithin for homeotropic alignment.

Linearly polarized light was incident vertically first upon the photochromic plate to avoid the distortion of the polarization plane of the actinic light by the passage through the anisotropic mesophasic layer. The photoinduced azimuthal anisotropy was checked by measuring the intensity of a probing He-Ne laser beam through the cell and a crossed polarizer as a function of the rotation angle of the cell. The cell axis is tentatively defined as the direction of the longer sides of the rectangular cell. The angle θ stands for the angle between the cell axis and the polarization plane of the actinic visible light while ϕ means the angle contained by the cell axis and the polarized light plane of the monitoring He-Ne laser beam, as illustrated in Fig. 1.



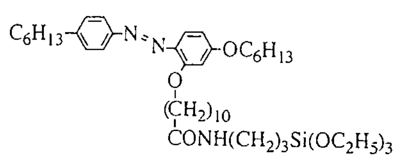


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FIGURE 1 Definition of rotation angles θ and ϕ between the cell axis and the light plane axes.

REGULATION BY LATERALLY ATTACHED AZOBENZENE

Our basic idea to realize a persistent homogeneous alignment is to excite azobenzenes attached on a substrate surface with linearly polarized visible light for the n-π^* transition to yield a photostationary state consisting of major amount of trans isomer. If the reorientation of surface azobenzene takes place, liquid crystal molecules may rearrange unidirectionally due to the specific interaction between the azobenzene units and liquid crystal molecules at boundary region. Thus, molecular design was undertaken to fulfill the following conditions; the chromophore mimics the size and shape of nematic liquid crystal, and the linkage of the chromophore is made lateral so that the long axis of the chromophore is preferentially oriented in parallel with respect to a substrate surface.

We prepared an azobenzene (1) substituted with two long chains, hexyl and hexyloxy, at the p-positions and a triethoxysilyl residue at the o-position of the molecule through a spacer unit to attach the command molecule laterally onto substrate quartz plate.[6] A hybrid cell

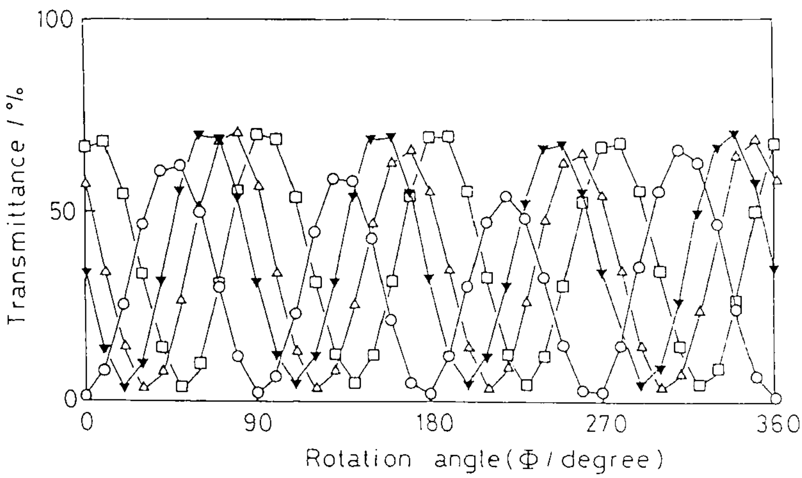


FIGURE 2 Angular (ϕ) dependence of transmittance of He-Ne laser beam through the cell after exposure to linearly polarized visible light with polarization plane of θ = 0° (-○-), -30° (-▼-), -45° (-△-) and -60° (-□-), respectively.

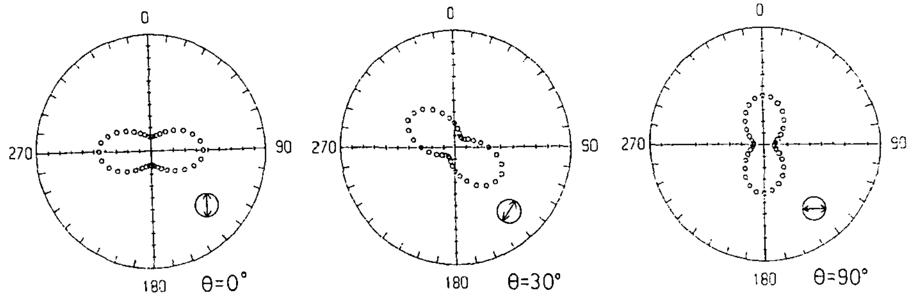


FIGURE 3 Polar diagrams for the cell filled with DON-103 containing 1 wt% of a dichroic dye after irradiation with polarized light of various plane angles.

filled with DON-103 was bright between two crossed polarizers, supporting the planar mode induced by the laterally attached azobenzene.

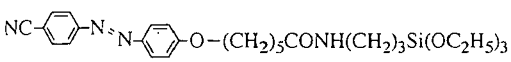
The azimuthal reorientation was caused photochemically and accelerated above the transition temperature (T_{NI}) of liquid crystal between nematic and isotropic phases. Fig. 2 shows the birefringence patterns of the cell after irradiation with the polarized visible light of various polarization angles (θ) at 100℃ The direction of in-plane alignment can be controlled by selecting suitable θ. The exposure energy required for the in-plane reorientation was considerably reduced at temperatures higher than T_{NI}. The cell demonstrated marked stability of the alignment toward heat treatment; no birefringence alteration was observed even after heating at 100℃ for 1 hr.

The direction of the photoinduced homogeneous alignment was determined by measuring photodichroism of dichroic dye molecules dissolved in the nematic liquid crystal to fabricate a guest-host cell. The dye molecules align parallel with respect to the liquid crystal molecules. Fig. 3 presents the absorbances at 625 nm of polarized probe light as a function of rotational angle of the irradiated cell, indicating that the alignment direction is perpendicular to the polarization plane of the actinic light.

Exposure energies for alignment of the G/H cells were measured as follows. The cells were initially irradiated with the polarized light to attain homogeneous alignment, followed by subsequent illumination with the same light at various temperatures after rotating the polarization plane at 90° . The results showed again that the photoinduced reorientation of liquid crystal is enhanced drastically above T_{NI} .

ALIGNMENT REGULATION BY p-CYANOAZOBENZENES

In order to examine the validity of the molecular design to attach an azobenzene on substrate surface laterally, a p-cyanoazobenzene moiety was employed as the command-molecular unit because the trans form attached onto



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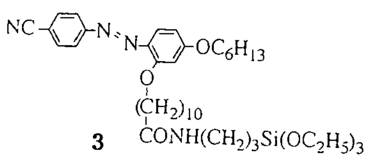

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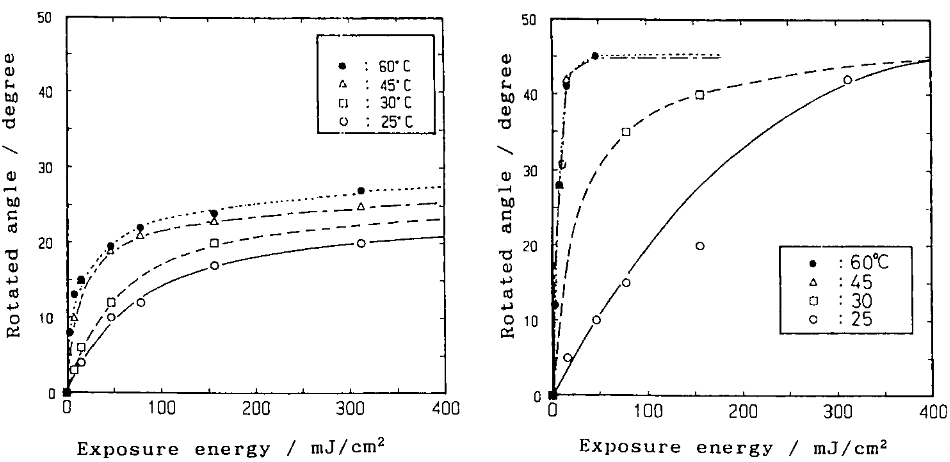


FIGURE 4 Rotated angles of homogeneous alignment direction after illuminating a cell (left side; modified with 2, right side; modified with 3) with polarized visible light as a function of exposure energy and cell temperature.

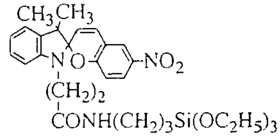
the substrate surface affords planar mode even though the groups are attached in a conventional head-on fashion.[7] A triethoxysilyl residue was introduced at the o and p-position (2 and 3), respectively, to modify quartz surfaces and to fabricate cells with use of EXP-CIL.

It was confirmed that the photoinduced reorientation of EXP-CIL molecules is induced in both cells when they are irradiated to linearly polarized visible light. The photoinduced reorientation of the liquid crystal was evaluated by the following procedure; the cells were exposed to the linearly polarized light for the homogeneous alignment in advance and subsequently illuminated with the light at a temperature higher than T_{NI} after rotating the polarization plane at 45° to follow the rotated angle of reoriented alignment direction. Remarkable difference in photoresponsive behaviors between both cells was observed in the following points, as demonstrated in Fig. 4. First, the exposure energies for the reorientation is much reduced when the azo-moiety is introduced by the side-on manner. Second, the rotated angles are leveled off at the maximum angle 45° for the cell modified with the side-on type 3 whereas the head-on type (2) cell exhibits much less rotated angle of the reorientation. These support obviously that the side-on type attachment of command molecules on substrate surfaces is more effective for the photoalignment.

SPIROPYRAN AS COMMAND MOLECULE

The extension of the photoregulation of liquid crystal alignment by molecules other than azobenzenes is closely related not only with the elucidation of working mechanism, but also with the practical applications. An alternative command molecule for the azimuthal alignment is a spiropyran which displays reversible electrocyclic reaction based on a 6π-electron system.

A silica surface treated with a spiropyran (4) brings about a planar alignment before and after UV irradiation so that no evident alignment alteration was induced photochemically.[8] However, when actinic UV light is linearly polarized, a plate modified with 4 generated the azimuthal anisotropy of a liquid crystal layer.[9] The cell temperature above T_{NI} played an essential role in the photocontrol also in this case.



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PHOTOALIGNMENT MECHANISM

The photoinduced emergence of the azimuthal anisotropy by means of the surface azobenzenes can be interpreted as follows. Continuous irradiation with polarized visible light leads to the selective excitation of the azo-chromophores, which have a transition moment parallel with respect to the polarization plane of actinic light, to lead to the molecular reorientation of the chromophores as a result of the accumulated E/Z photoisomerization. This was supported by the observation of photodichroism of the azobenzene (1) after polarized light irradiation.[6] Liquid crystal molecules at a boundary region rearrange parallel to the aligned azobenzene units on the surface due to the side by side molecular interaction to form homogeneous alignment of the bulk mesophase. This situation may be reasonably illustrated in Fig. 5.

The same mechanism can be applied to the photoalignment by spiropyran units. Because the photochromic units are attached onto the surface at the nitrogen atom through a spacer, the long molecular axis of the chromophore containing two spiro-ring systems seems to be approximately parallel to the surface. UV light at 365 nm is absorbed by both the spiropyran moiety and the corresponding merocyanine

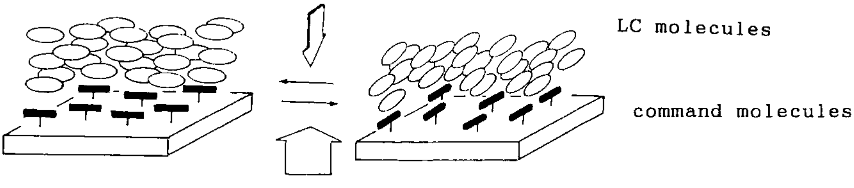

FIGURE 5 Illustrative representation of the in-plane reorientation of liquid crystal molecules.

forms. Thus, the chromophores on the surface may reorient under illumination with the polarized light as a result of the accumulation of the photochromic reaction so that the direction of the long molecular axis is set vertical to the polarization plane. This brings about the homogeneous alignment quite similarly to the azobenzene cases (Fig. 5).

CONCLUSION

Stable homogeneous alignment of nematic liquid crystals is caused by irradiating a substrate quartz plate which is covered with azobenzenes and a spiropyran molecular layers. Although further mechanistic studies on the photoalignment are needed, requirements for the photoinduced in-plane alignment may be summarized as follows.

(1) Photochromic units attached on substrate surface should produce planar alignment before and after photoirradiation.

(2) Linearly polarized light is absorbed by both isomeric forms of surface photochromic units to accumulate the molecular reorientation.

(3) Cells are favorably heated above T_{NI} to enhance the homogeneous alignment.

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