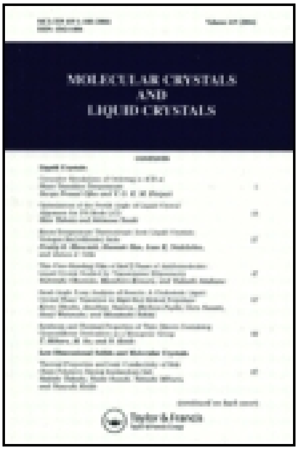

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NEMATIC HOMOGENEOUS ALIGNMENT REGULATED BY THE POLARIZATION PHOTOCHROMISM OF SURFACE AZOBENZENES

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Abstract Alignment modulation of a nematic liquid crystal was performed by a polarization-selective photochromic reaction of surface azobenzenes. The alignment was changed from an initial perpendicular state to a homogeneous planar state by exposure to the linearly polarized UV light. The induced homogeneous axis was perpendicular to the electric polarization of the reaction light. Rotation of the homogeneous axis was demonstrated by changing the light polarization, and the corresponding relaxation time was measured by laser pulse experiments.

INTRODUCTION

Photochemical transformation of molecules could induce a drastic structure-change of the neighboring organized molecular system. We have already demonstrated that the alignment of a nematic liquid crystal (LC) is controlled between the homeotropic state and the planar state by the photochromic *trans-cis* isomerization of surface attached azobenzene (Az) molecules (figure 1)[1-4]. The natural texture of the induced planar alignment was marbled or schlieren, suggesting lack of any particular orientation axes in the planar phase, as long as the cell was exposed in ordinary way. However, as described in the present report, the orientation order of the planar phase was considerably improved by changing the excitation light characteristics[5]. Highly homogeneous alignment was obtained by exposure to the linearly polarized UV light.

EXPERIMENTAL

The photoresponsive LC cell was fabricated by sandwiching a nematic mixture (Rodic DON103, K-290-N-344-I) between a pair of modified glass plates with 8μm spacers. For investigation of the align-

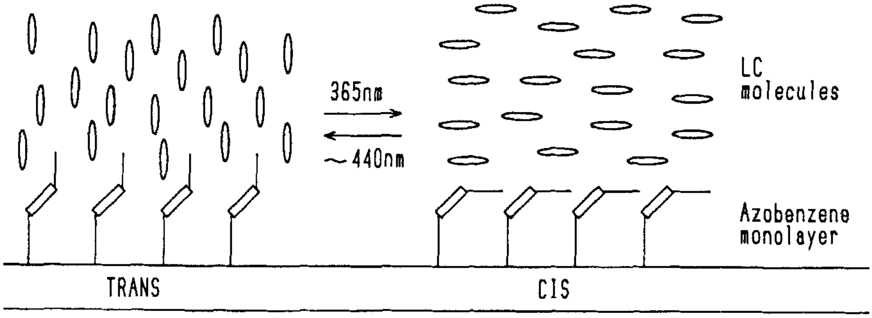
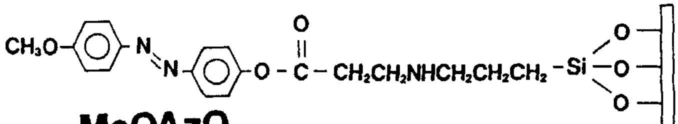
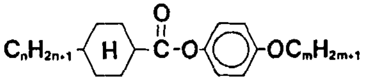


Figure 1 Illustrative representation for the regulated alignment change of a nematic liquid crystal by the photochromic reaction of surface azobenzenes.

ment axis, a guest-host (GH) cell containing 1.0 wt% of a dichroic dye (Nippon-Kayaku LCD118) was used. Structures of chemicals and surface Az are shown in figure 2. A 500W high-pressure Hg arc lamp was used with optical filters to obtain UV (365nm) and visible (440nm) reaction-light, and with a Glan-Thompson-Taylor prism polarizer for linearly polarized exposure. Experimental configuration was illustrated in figure 3.



MeOAzO



DON103 (n,m = 3,2 - 4,5 - 5,1)

Figure 2 Structures of surface azobenzene MeOAzO and nematic DON103

RESULTS AND DISCUSSION

Figure 4 shows the polarizing micrographs of the photoresponsive LC cell. On preparation of the cell, the LC alignment was homeotropic (A). Exposure of nonpolarized UV light resulted an inhomogeneous multi-domain texture suggesting low orientational order of the parallel plane (B), and the alignment returned to the homeotropic after subsequent visible exposure. However, it was found that an uniaxially oriented parallel phase was developed by applying the linearly polarized UV light (C).

From the results of angular dependent transmittance of the GH cell (figure 5), the induced axis was found to be perpendicular to the electric polarization of the UV light. Besides, it is possible to rotate the homogeneous axis by changing the light polarization.

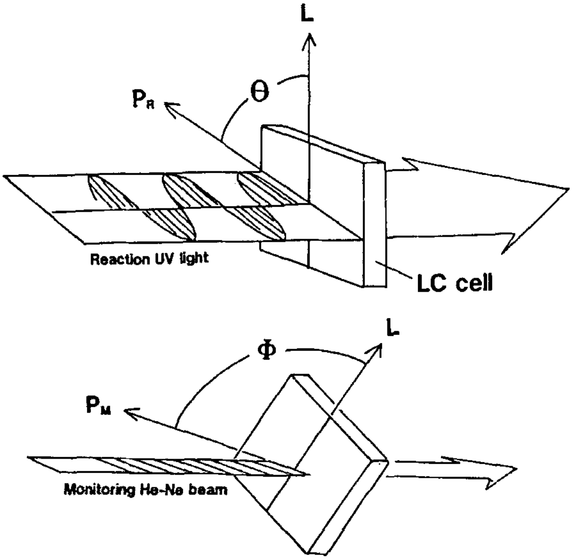


Figure 3 Configuration for polarized light exposure. P_R: electric polarization of the reaction light, P_M: polarization of the monitor light, L: tentative axis of the cell, θ : polarization angle of excitation, ϕ : rotation angle of the cell.

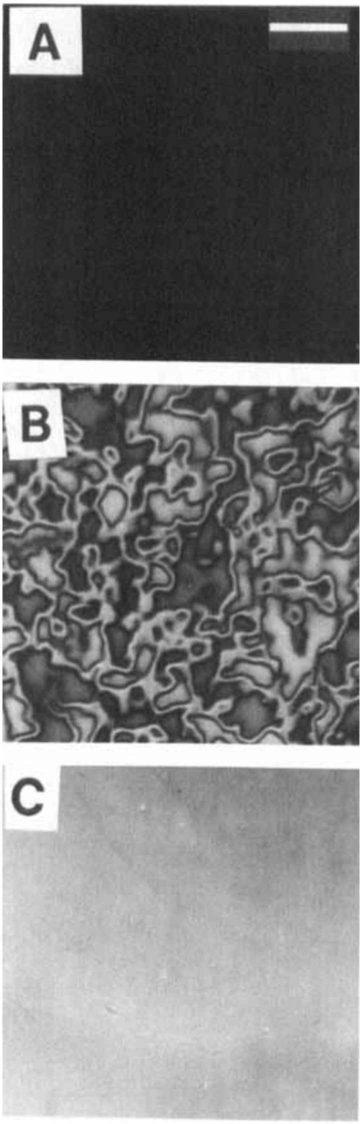


Figure 4 Polarizing micrographs of the photoresponsive LC cell. The bar represents 100μm.

A) On preparation.
B) After ordinary exposure with non-polarized UV light.
C) After exposure with the linearly polarized UV light.

When the LC phase did not contain the dichroic dye, the induced homogeneous axis was not exactly perpendicular to the polarization. This inconsistency is probably brought about by the photochromic reaction of the second Az surface at the outlet of the reaction light. In the GH cell, the second Az surface can not absorb the reaction light due to the large absorbance of the doped dye, and the LC alignment is controlled only by the first Az surface at the intake of the reaction light. Since the reaction light reaches the second Az surface with changing its polarization characteristics in the undoped LC cell, each Az surface should suffer individual photochromism to present complicated dependence of the LC alignment on the polarization. This complication is avoidable when a hybrid LC cell is used instead, the second surface of which is replaced to a photoinert substrate surface such as an

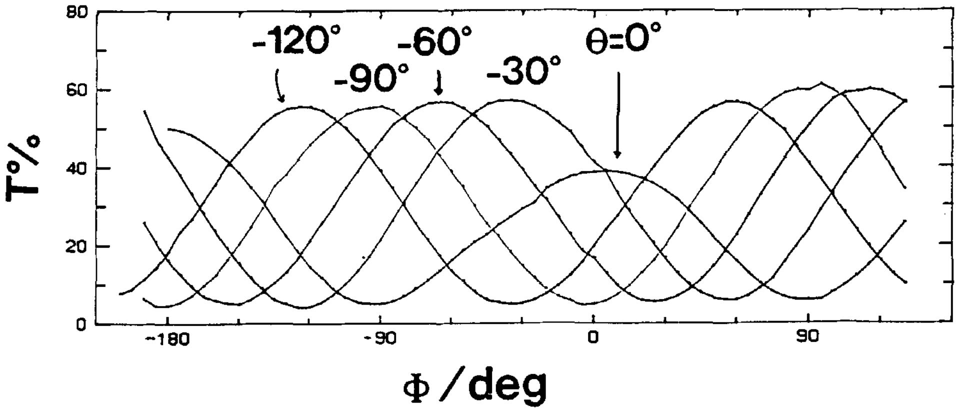
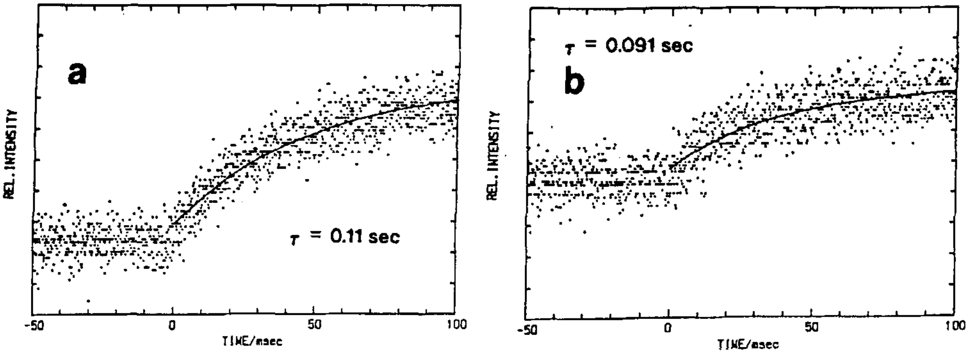


Figure 5 Angular dependent transmittance of homogeneously aligned MeOAzO/MeOAzO GH cell at 633nm induced by linearly polarized irradiation with various polarization angles *θ* .



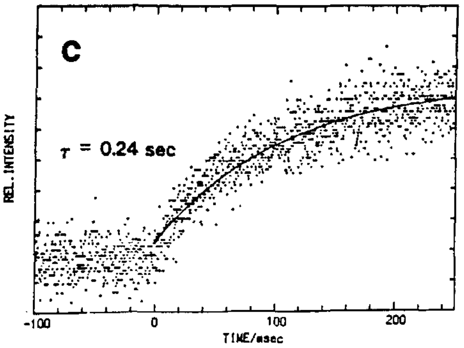


Figure 6 Alignment relaxation after the XeCl-DMQ laser pulse.
a) H→P(random) alignment change induced by non-polarized pulse.
b) H→P(homogeneous) alignment change induced by polarized pulse. Induced axis is in the diagonal position.
c) P(homogeneous)→P(homogeneous) rearrangement by rotating the laser polarization 45°. Induced axis is in the diagonal position.

octadecylsilylated (ODS) surface.

Alignment relaxation constants were analyzed by means of laser pulse experiments to be 110msec for the H→P(random) change, 90msec for the H→P(homogeneous) change, and 240msec for rotation of the homogeneous axis 45° to the original, respectively (figure 6). All the relaxation curves were well explained by the monoexponential function. Probably, the homogeneous alignment is not produced through the random parallel alignment, but directly from the perpendicular state, since the H→P(homogeneous) relaxation constant does not involve contribution from inner plane rearrangement.

Present photoinduced homogeneous orientation should originate from a polarization-selective photochromic reaction (polarization photochromism)[6,7] of surface Az molecules. According to semiempirical LCAO-SCF-CI calculations[8], both the lowest $\pi-\pi^*$ transition-vector of *trans*-Az and that of *cis*-Az are parallel to their -N=N- bond axes. Along with the polarized UV exposure to the lowest $\pi-\pi^*$ transitions, the average alignment of Az molecules in terms of -N=N- axis should become perpendicular to the incident polarization plane due to their polarization-selectivity on light-absorption. LC molecules tend to align their long axes parallel to those of surface *trans*-Az molecules[9-11]. On the other hand, ordered structures of LC phase are often destroyed by *cis*-Az molecules[12] due to their low compatibility. Consequently, it is most likely that *cis*-Az turns the nematic phase from the perpendicular alignment to the parallel alignment while *trans*-Az provides the specific alignment axis to the parallel phase, respectively.

CONCLUDING REMARKS

Induction and modulation of the molecular alignment axis have been performed in our photoresponsive LC system by the action of the light. Induced anisotropy of the LC system is significantly high compared with that of polymer based systems.[13-15] The advantage of the LC system is its self-organizing structure. This amplifies small changes in surface morphology and will be utilized for future molecular devices. Further experiments are in process to clarify the mechanism of photomodulated LC rearrangement.

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