CHEMISTRY LETTERS, pp. 1063-1066, 1992. © 1992 The Chemical Society of Japan

Photocontrol of In-plane Alignment of a Nematic Liquid Crystal by a Photochromic Spiropyran Monolayer Absorbing Linearly Polarized Light

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Azimuthal anisotropy of a nematic liquid crystal alignment was caused by exposing 6-nitrospirobenzopyran monolayer to linearly polarized UV light. The photo-induced in-plane alignment was scarcely altered after prolonged storage at an ambient temperature.

The alignment of liquid crystals (LCs) is governed by the boundary region between LC layer and substrate surfaces.1) This implies that the LC alignment can be controlled by the regulation of surface properties. Indeed, the alignment alteration of nematic LCs between homeotropic and planar states is reversibly induced by the geometrical photoisomerization of some photochromic monolayers2) called "command surfaces." Such a monolayer-mediated photocontrol has been expanded to the in-plane LC alignment alteration triggered by action of linearly polarized UV light on an azobenzene monolayer.3) This letter concerns an alternative command surface which consists of a photochromic spiropyran monolayer and regulates reversible in-plane orientation of a nematic liquid crystal.

The surface modification of quartz plates (1 x 3 cm^2) with a 6-

nitrospiropyran (SP) having triethoxysilyl group has already reported in our previous paper.[4] We have employed here a nematic LC (Rodic/EXP-CIL: T_{NI}=32.6 °C) which is a UV-transparent mixture of a cyclohexanecarboxylate and two cyclohexylcyclohexenes. The LC suspending spherical glass spacers of 5 μm diameter (SP-50F: Tokuyama Soda Co. Ltd.) was put between the surface-modified plate and a quartz plate, the surface of which was modified with lecithin for homeotropic alignment to afford a hybrid cell.

The hybrid cell was bright between crossed polarizers, indicating that the surface modified with SP brings about a planar mode. UV Irradiation resulted no transmittance alteration of monitoring linearly polarized light, confirming our previous observation that alignment regulation between homeotropic and planar modes could not be generated by the photochromic reaction in the monolayer.[4]

It was found that linearly polarized UV light at 365 nm from a 500 W high pressure mercury arc causes the emergence of azimuthal anisotropy of the mesophase due to the in-plane alignment regulation of the LC molecules.

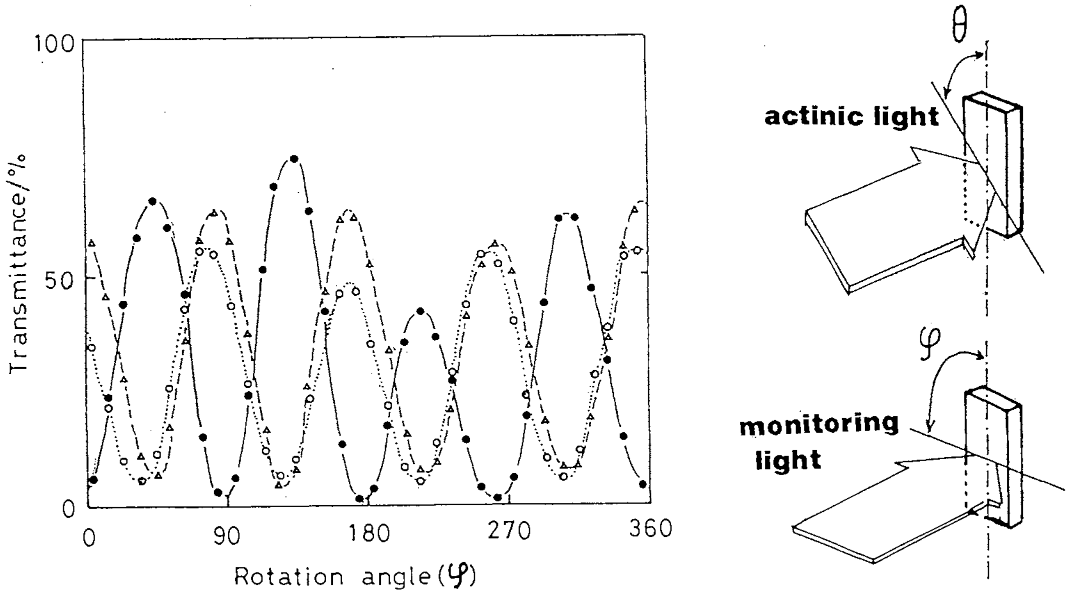

Fig. 1. Transmittance of linearly polarized, monitoring He-Ne laser beam as a function of rotation angle (φ) of the LC cell exposed to actinic UV light with various polarization plane angle (θ) (—●—; θ=0°, --Δ--; θ =+45°,···○···; θ=-45°).

The cell temperature above T_{NI} played an important role in the photocontrol; the exposure at an ambient temperature (about 20°C) gave rise hardly to the in-plane alignment alteration.

The rectangular cell was placed on a hot plate at 54°C and exposed to the linearly polarized UV light. Fig. 1 shows the angle (φ) dependence of transmittance of a linearly polarized He-Ne laser beam through the cell and a crossed polarizer in this sequence. φ is defined as the angle between the light plane of a monitoring He-Ne laser beam and the cell axis, which is here defined as that parallel to the long sides of the cell. When the polarization axis of the actinic light is set in the same direction (θ = 0°) as the cell axis, the minimum transmittance appeared approximately at φ= 0°+ 90°x n, indicating homogeneous alignment. The rotation of the actinic light plane from θ= 0° to +45° resulted in the alteration of the angle (φ) dependence so that the minimum transmittance was observed at φ= 45°+ 90° x n. The cell was again irradiated with the linearly polarized light with θ= -45°. As seen in Fig. 1, the angle dependence was almost unchanged.

As mentioned in our previous paper, the SP ring on a quartz plate opens partially even in the dark due to highly hydrophilic microenvironment on quartz surfaces.[4)] This implies that the photoselection may also take place in the ring closure of the merocyanine form upon exposure to polarized visible light. Contrary to our expectation, no distinct photocontrol of the azimuthal anisotropy of the mesophase was attained upon exposure to the polarized visible light (>430 nm). This confirms

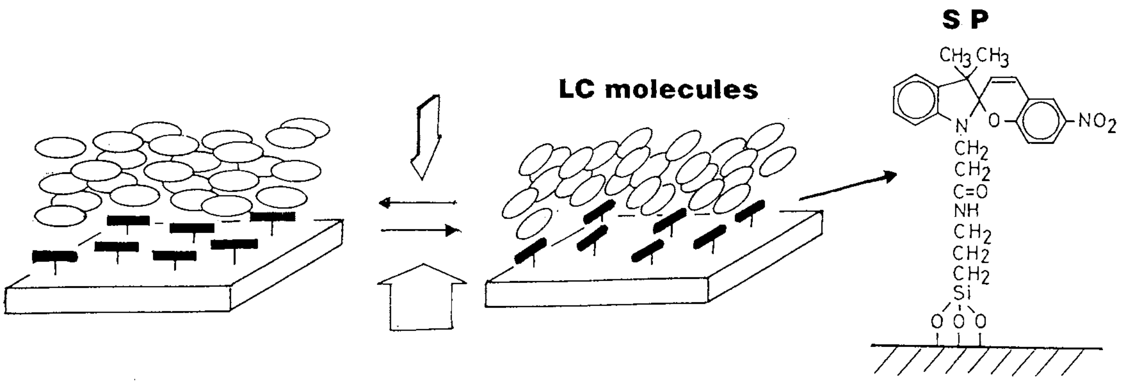

Fig. 2. Illustrative representation of in-plane LC alignment regulation.

that the photoselection takes place during the course of the ring opening.

Because the photochromic unit is attached to quartz surface at the nitrogen atom through a spacer, the long axis of the chromophore containing two ring systems seems to be approximately parallel to the surface. This situation may lead to the LC planar mode because of side by side interaction between SP units and LC molecules. The ring opening of the spiropyran is initiated by photon absorption of the "right" side of SP, 2H-nitrochromene moiety, which possesses a conjugated π-electron system quite similar to p-nitroanisol. Thus, the direction of the transition moment of the chromophore is parallel to the long axis of the photochromic skeleton, and the excitation with the linearly polarized UV light brings about preferential consumption of SP units, the long axis of which is parallel to the polarized light plane. The photoselection induced by the polarized UV light accumulates the reorientation of the SP units so that the direction of the long molecular axis is placed vertical to the polarized light plane to result in the unidirectional reorientation of the LC molecules, as illustrated in Fig. 2. The role of the thermal reversion of the photomerocyanine in the photoselection is not clear at present.

The photoinduced azimuthal anisotropy was stable on prolonged storage at an ambient temperature and even under room light. These facts suggest the potential usefulness of this type of photosensitive LC devices for a rewritable optical information storage.

References

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(Received April 1, 1992)