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Alignment Photocontrol of a Liquid Crystal by Spirooxazine Monolayers

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In purpose to enhance the sensitivity of liquid crystal (LC) photocontrol by spirooxazine (Sox) monolayer, we report here the effect of N-alkyl residues of Sox on the photochromic behavior in monolayers and their ability to control LC alignment.

Keywords: Alignment; Photocontrol; Liquid Crystal; Spirooxazine

INTRODUCTION

Whereas spirooxazine derivatives display excellent photofatigue resistance, the photochromic Sox / photomercocyanine (PMC) system has attracted no marked interest in applying to photomemory because of the rapid thermal bleaching. We reported previously that thermally stable in-plane alignment of nematic liquid crystals (NLCs) is generated by the irradiation of monolayers (1 in Figure 1) of Sox chemisorbed on a surface of a silica substrate with linearly polarized light while the thermal reversion takes place rapidly.¹⁾

Consequently, the photogeneration of the homogeneous alignment required an exposure period hundreds-times longer than that for azobenzene-modified substrate plates, though no optimization was carried out.²⁾

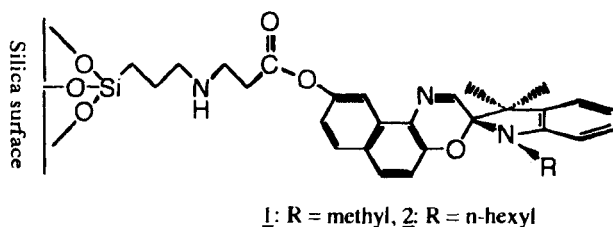


FIGURE 1 Structures of Sox attached to a silica surface.

One of optimization technique is modifying chromophore structure compatible with that of LC molecule, namely, consists of rigid core and flexible side chain. According to the hypothesis, we report here the effect of N-alkyl residues of Sox on the photochromic behavior in monolayers and their ability to control LC alignment.

EXPERIMENTAL

Materials and cell fabrication

Both **1** and **2** were prepared by Michael addition of the corresponding 9'-Acroyl Sox and 3-aminopropyltriethoxysilane attached on silica surface in advance. Then, the Silica plate was soaked in Ethanol solution of Sox and heated in an oven at 120°C for 20 min. Sox attached plate was ultrasonicated with chloroform twice.

LC hybrid-type cells were assembled by sandwiching a nematic LC, (EXP-CIL of $T_{NI} = 32.6^{\circ}\text{C}$) doped with or without a dichroic guest dye (LCD-118) between a silica plate modified with Sox and a plate modified with lecithin.

Measurement

The density of Sox on Silica surface was calculated from Absorbance of the plates and ϵ of Sox.

Photoisomerization of 1 and 2 was measured with a Hewlett-Packard diode array spectrometer 8453. irradiated 365 nm UV light with Ushio high pressure mercury light at room temperature. The results are summarized in table 1.

Estimations of LC alignment were carried out according to our previous procedure². As initial LC directions of the cells were heavily effected by direction of LC dipping, the photo-sensitivity of cells were estimated form reorientation measurement. After LC was aligned along with the direction of polarized light, the direction was changed by the light that polarized direction was different from former light. The direction changes were plotted vs. irradiated time.

RESULT and DISCUSSION

Photoisomerization

TABLE 1. Characterization of Sox modified silica surfaces.

	Surface density of SOx (/ nm ²)	Absorption of PMC (A, ($\lambda = 611\text{nm}$))	half decay time of PMC (sec)
1	6	0.0010	10
2	3	0.0015	20

A thermal decoloration rate of a monolayer of 2 was reduced approximately by half when compared with that of 1. The results may arise from the steric effect of hexyl group on the thermal reversion. Low density of Sox and slow decoloration late decrease the sensitivity of LC alignment control.

Liquid crystal photoalignment

The defects of aligned LC cell of 1 was not much different from 2.

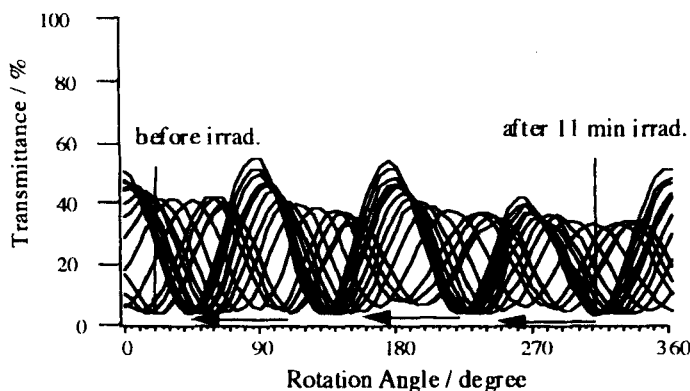


FIGURE 2. Angular dependence of transmitted light intensity of a monitoring linearly polarized He-Ne laser beam through a 1 and lecithin modified LC cell. Linearly polarized UV light was irradiated with polarization plane 50 degree direction for 0.5, 1, 2, 3, 4, 5, 7, 9, 11, 15 min. respectively.

Reorientation by polarized light which direction was different was shown in Figure 2. When the difference between the lights are small, LC direction shift keeping orientation. If the difference become 90 degree, alignment was disappeared and parallel orientation is appeared during the process.

Effect of alkyl side chain to the sensitivity As shown in Figure 3, the photo-reorientation of an LC filled in a cell modified with a monolayer of 2 proceeded three times faster than that of 1, suggesting that the longer alkyl chain plays a role in the enhancement of LC photoalignment due to interactions between the alkyl and LC molecules because measured photochemical property of surface attached 2 suppress Photocontrol of LC.

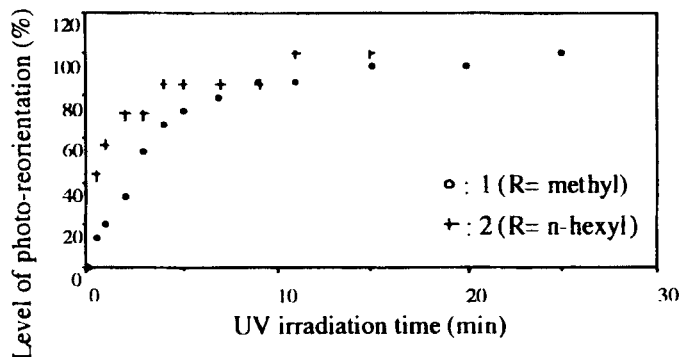


FIGURE 3 Photo-reorientation of LC in cells surface-modified with Sox upon irradiation with linearly polarized UV light.

Though the irradiated energy to control LC for the Sox cells is still much higher than that of azobenzene, this enhancement of sensitivity will contribute for the application of Soxs.

CONCLUSION

- 1 A thermal decoloration rate of a monolayer of 2 was reduced approximately by half when compared with that of 1.
- 2 The liquid crystal reorientation by the Sox 2 possessing n-hexyl group proceeded three times faster than that of 1.
- 3 The above result suggests that the longer alkyl chain plays a role in the enhancement of LC photoalignment due to interactions between the alkyl and LC molecules.

References

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