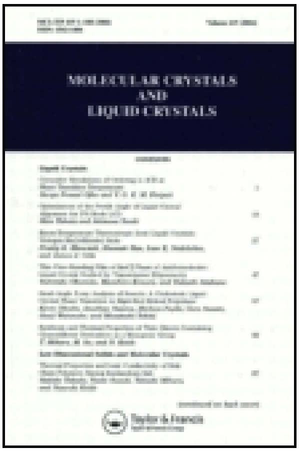

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Photoregulation of Liquid Crystal Alignment by Photoisomerizable Molecular Layers

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PHOTOREGULATION OF LIQUID CRYSTAL ALIGNMENT BY PHOTOISOMERIZABLE MOLECULAR LAYERS

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Abstract Linearly polarized UV light irradiation of a nematic liquid crystal cell assembled with a quartz plate surface-modified with a stilbene caused reversible reorientation of liqquid crystal molecules.

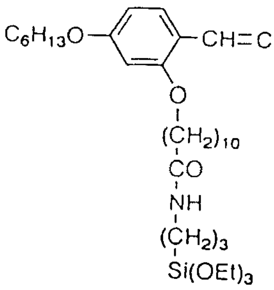
INTRODUCTION

Photoinduced liquid crystal (LC) alignment by photoisomerizations of chromophores on substrate surfaces has opened a way to novel photomemories and display devices.[1,2] Our work has revealed that in-plane LC alignment regulation can be achieved by the surface photoisomerization of azobenzenes with linearly polarized light (LPL).[3-4] The working mechanism has been assumed to be as follows. Linearly polarized light is absorbed by azobenzene with a transition moment parallel to the electric vector of actinic light to result in the molecular-axis-selective photoisomerization leading to the reorientation of chromophore units. This paper concerns the in-plane alignment photocontrol by the geometrical photoisomerization of stilbenes in order to confirm the working mechanism.

RESULTS

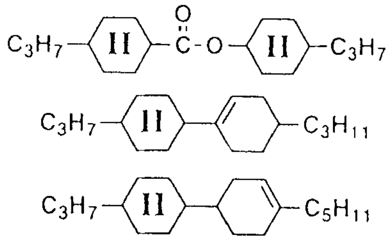
Synthesis and photochemistry

Our previous work showed that the attachment of azo-chromophores at the lateral position to a silica surface results in an effective alignment photocontrol.[4] Consequently, a triethoxysilyl residue is introduced at the o-position of stilbenes through a spacer to prepare two silylating reagents. They are substituted with alkyl group(s) at



StC4: R=H

C4StC6: R=C_4H_9



EXP-CIL

their p-position(s) in order to mimic the shape of LC molecules. The silylation of a quartz surface was carried out in a conventional way. An average area occupied by each olefinic chromophore on a quartz surface was estimated by UV absorption assuming that the absorption coefficients are not altered by the attachment to the surface. The surface occupied areas of C4StC6 and StC6 were 0.93 nm^2 and 0.85 nm^2 per molecule, respectively.

Under the present irradiation conditions, the stilbenes in solution reached a photostationary state within a few second, followed by the gradual oxidative cyclization to form phenanthrenes upon prolonged irradiation.[5] The formation of phenanthrene was detected by fluorescence and excitation spectra of an irradiated solution. Table 1 shows the dependence of isomer ratios of both stilbenes in photostationary states on irradiation wavelength. UV Exposure of stilbene-modified plates caused spectral changes quite similar to those in solutions.

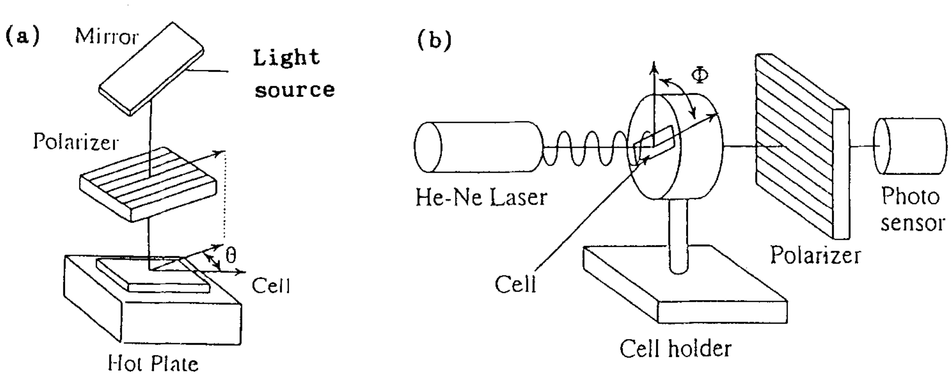


Fig. 1 Experimental setup for (a) polarized light irradiation and (b) evaluation of LC alignment.

Photoalignment

A hybrid cell was assembled by sandwiching an LC, EXP-CIL of T_{NI}=31.5 ℃, between a quartz plate surface-modified with a stilbene and a plate adsorbing lecithin for a homeotropic alignment. Irradiation of cells with LPL of an electric vector (θ) and evaluation of photoinduced alignment by measuring the transmittance of a polarized probing He-Ne laser light as a function of a rotational angle (ϕ) of the cell were carried out according to Fig. 1. Fig. 2 shows the results for the LC alignment in a cell made from a plate modified with the C4StC6 silylating reagent upon exposure to polarized 260 nm light at room temperature, as a typical example. There appears a pattern having valleys and peaks with a regular 90° separation, showing that the transmittance is a function of $\sin^2(2\theta)$. This means that uniaxial alignment was induced by LPL irradiation. The photoinduced alignment direction was determined to be approximately perpendicular to an electric vector of actinic light by measuring the dichroism of a dichroic anthraquinone dye dissolved in the LC.

Effect of wavelength

Each cell was irradiated first with monochromatic polarized light of θ = 0° for the initial homogeneous alignment until no marked altera-

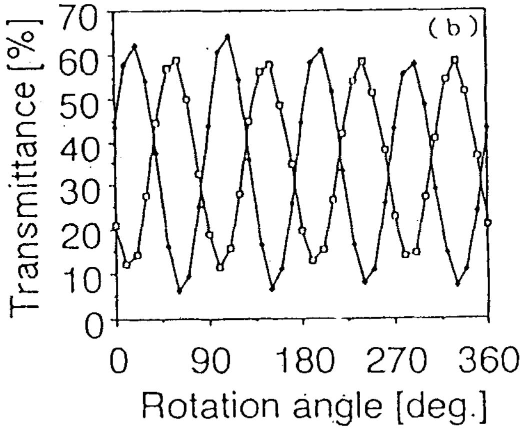


Fig. 2 Dependence of transmitted light intensity of a probing linearly polarized He-Ne laser beam through a photoresponsive cell surface-modified with C4StC6 after irradiation with 260 nm polarized light at θ=0° (-●-) and at θ=45° (-□-) as a function of a rotational angle (ϕ) of the cell.

tion was detected in the alignment by tracing the relationship between the transmittance and rotational angle (ϕ) of the cell. Subsequently, the cell was illuminated after setting the polarization plane of actinic light at $\theta = 45°$. After the completion of the second alignment, the polarization plane was rotated at $\theta = 70°$ to give rise to the third reorientation. The results are compiled in Table 1. Here, $\Delta\theta$ and $\Delta\phi$ denote differences in the polarization plane angle of actinic light and in the alignment direction between the initial and the subsequent irradiation, respectively.

Observation with a polarized microscope showed that a mesophase layer contains optical defects owing to disclinations and partial incompleteness of the uniaxial alignment. They caused a leakage of monitoring polarized light at a crossed position of a cell to increase the minimum transmittance. Thus, a contrast defined as T_{max}/T_{min}, where T_{max} and T_{min} stands for the maximum and minimum transmittances of probing light, respectively, is assumed to be a measure to evaluate the optical quality of a photoirradiated cell. As given in Table 1, it is clear that irradiation with 330 nm light gives rise to a poor contrast for cells modified with both stilbenes while 260 nm irradiation is favorable for a higher contrast.

DISCUSSION

The perpendicular LC reorientation photoinduced by the surface stilbenes is in line with the results obtained by azobenzene chromophores. Just as in the case of azobenzenes, the transition moment of stilbene lies parallel to the longitudinal molecular axis so that the rearrangement of the chromophore takes place to result in the perpendicular reorientation as a result of the repetition of the geometrical photoisomerization.

The wavelength dependence on the contrast summarized in Table 1 can be reasonably interpreted by the assumption that the LC alignment arises from the perpendicular reorientation of the trans-stilbene units on a surface by polarized UV light. The photoisomerizable units trigger the in-plane LC reorientation of when the rod-like trans-isomer is a major component under the illumination condition.

Table 1 shows furthermore that the effect of the introduction of butyl group on the stilbene moiety is twofold. First, the presence of

Table 1 Photoalignment properties of LC cells exposed to polarized UV light at various wavelengths

Stilbene	Irradiation wavelength (nm)	Trans:Cis[a]	Exposure energy (J/cm^2)	Aligned direction[b] $\Delta\theta$	$\Delta\phi$	δ	Contrast T_{max}/T_{min}
StOC6	260	42 : 58	0.17	0	-		3.9
			0.51	45	44	1	
	290	34 : 66	1.8	-	-		3.9
			3.2	45	32	13	
			2.0	70	42	28	
	330	26 : 74	1.7	-	-		2.8
			3.4	45	10	35	
			3.4	70	18	52	
4StOC6	260	77 : 23	0.21	-	-		3.2
			0.53	45	39	6	
			0.42	70	65	5	
	290	45 : 55	0.094	-	-		4.5
			0.58	45	45	0	
			0.83	70	68	2	
	330	27 : 73	1.7	-	-		2.2
			10.0	45	35	10	
			6.8	70	49	21	

a) In a photostationary state in an ethanolic solution. b) See text. The values are within ± 2° .

p-butyl residue leads to the marked reduction of both the exposure energy for the reorientation and the delay of reorientation direction (δ). This is in particular considerable when irradiation is made with 290 nm light. These imply that the butyl residue plays a role in triggering the reorientation of liquid crystal molecules possibly because of mimicking effect of mesogenic structure.

Table 1 also indicates that $\Delta\theta$ does not always be equal to $\Delta\phi$ to result in the reorientation delay which depends on the irradiation wavelength and the structure of the stilbene. Here, δ is defined as a delay in the reorientation direction of LC and equal to a difference between $\Delta\theta$ and $\Delta\phi$. The δ value is zero within experimental errors when a cell made from a plate modified with StC6 is illuminated again with 260 nm light after changing the polarization plane of actinic light. In contrast to this, δ becomes much larger when a cell was exposed to light of wavelengths at 290 nm and 330 nm, respectively. This results stress the critical role of the trans isomer in the LC alignment control.

CONCLUSION

Stilbenes can command the in-plane LC reorientation. The efficiency of the photoalignment control is expressed as the contrast (T_{max}/T_{min}) as well as the reorientional angle shift (δ) and influenced considerably by the irradiation wavelength. The photoinduced homogeneous alignment favors the preferential formation of the trans isomer in a photostationary state. This implies that the LC reorientation is triggered by the trans isomers on a substrate surface. The presence of butyl residue at a p-position of stilbene moiety is also of a significance for enhancing the photoalignment efficiency.

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