Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Ichimura, Kunihiro , Tomita, Hidetoshi and Kudo, Kazuaki(1996) 'Command surfaces 14 [1]. Photoregulation of in-plane alignment of a liquid crystal by the photoisomerization of stilbenes chemisorbed on a substrate silica surface', Liquid Crystals, 20: 2, 161 — 169

To link to this Article: DOI: 10.1080/02678299608031122

URL: http://dx.doi.org/10.1080/02678299608031122

LIQUID CRYSTALS, 1996, VOL. 20, NO. 2, 161–169

Command surfaces 14 [1]. Photoregulation of in-plane alignment of a liquid crystal by the photoisomerization of stilbenes chemisorbed on a substrate silica surface

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(*Received 1 July 1995; accepted 6 September 1995*)

Stilbenes were attached to a quartz surface at their 2-position by silylation through a spacer to determine the capability to regulate an azimuthal alignment of a nematic liquid crystal by irradiation with linearly polarized light. Liquid crystal molecules aligned perpendicular to the direction of polarization plane of the actinic light, just as in the case of surface azobenzenes. The efficiency of the photoregulation was influenced by excitation wavelength and hence related with an *E*/*Z* isomeric ratio in a photostationary state. The irradiation with 260 nm polarized light resulting in the *E*-isomer as a major component in the photostationary state gave better optical quality of a photoaligned texture when compared with 330 nm irradiation, suggesting that the orientation of liquid crystals is induced by the rod-like *E*-isomer. Discussion was made on the possibility of the role of phenanthrenes, which were formed upon prolonged irradiation, in the liquid crystal photoalignment.

1. Introduction

The azimuthal photoregulation of liquid crystal (LC) alignment has been achieved by the irradiation of photoactive substrate layers with linearly polarized light (LPL) [1–7]. This surface-assisted alignment regulation is assumed to involve the following processes; the LPL irradiation of the photochromic molecules localized at a topmost surface layer of substrate plates leads to the reorientation of LC molecules surrounding the photoactive units, followed by the rearrangement of the bulk LC. This technique has been attracting particular interest from a practical viewpoint because of a potential value for erasable optical information recording driven by a single light source and for development of various optical elements displaying a photo-optical effect [8]. A persistent LC alignment achieved by the LPL irradiation provides a procedure to produce rubbing-free LC aligning membranes which are key materials in LC device technologies [9]. In order to present the scope and limitation of LPL-sensitive LC systems, systematic studies are required to obtain further insight into the working mechanism and to overcome various problems which stand in the way of practical applications. One of the ways to obtain further information concerning LPL-sensitive LC systems involves the development of photochromic molecules which are able to command the reorientation of LCs.

Azobenzenes [2–4] and a spiropyran [10] have been reported to be active to LPL-induced LC alignment. Preparation of command surfaces based on this type of photoisomerizable units has been made by dissolving azo-dyes in polymeric thin films [2, 6], by attaching azobenzenes to the surface of a silica plate [3, 4] or a poly(vinyl alcohol) film [11], and covering a substrate plate with a polymer substituted with azobenzenes in the side chains [12, 13].

This paper concerns the in-plane photocontrol of LCs by the geometrical photoisomerization around the C=C double bonds of stilbenes. Stilbene photoisomerizes through its excited state(s) with a twisted conformation and displays a drastic change in the molecular structure between the rod-like and bent shapes [14]. The *E*/*Z*-photoisomerization behaviour is quite similar to that of azobenzene except of the thermal stability of the *Z*-isomer. Here we report that the in-plane alignment regulation is achieved by modifying a silica surface with stilbene derivatives and that the photo-induced alignment behaviours are affected not only by the molecular structure of the chromophore, but also by the excitation wavelengths.

2. Experimental

2.1. *Materials*

A nematic LC, EXP-CIL (**1**), was kindly supplied by Rodic Co., Ltd and mixed with spherical glass spacers

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of a 5 µm diameter to adjust the cell gap. A diaminoanthraquinone dye (**2**) was a gift from Nippon Kayaku Co., Ltd (see figure 1).

2.2. *Synthesis*

2.2.1. *2-Hydroxy-4-hexyloxybenzaldehyde*

A solution of 1-bromohexane (5·00 g) and 2,4-dihydroxybenzaldehyde (5·90 g) in 20 ml of DMF was stirred at 65°C for 7 h in the presence of potassium carbonate (5·20 g). The reaction mixture was diluted with a mixture of hexane and ethyl acetate and extracted with a dilute aqueous solution of sodium hydroxide. The organic layer was washed with water and dried over magnesium sulphate. After removal of the solvents, the desired product, as a colourless oil, was isolated by column chromatography on silica gel with the use of a 9 : 1 (v/v) mixture of hexane and ethyl acetate as eluent in a 30 per cent yield. ^{1}H NMR (CDCl$_3$):δ (ppm): 0·9 (t, 3 H, CH$_3$), 1·15–2·2 (m, 8 H, CH$_3$), 4·0 (t, 2 H, ArOCH$_2$), 6·3–6·7 (m, 2 H, Ar–H), 7·4 (d, 1 H, Ar–H), 9·7 (s, 1 H, CHO). IR (neat): 2950, 2920, 2850, 1640 cm^{-1}.

2.2.2. *11-(2-Formyl-5-hexyloxyphenoxy)undecanoic acid*

To a solution of 2-hydroxy-4-hexyloxybenzaldehyde (3·73 g) and tetrahydropyranyl 11-bromoundecanoate (5·87 g) in 15 ml DMF was added potassium carbonate (3·50 g). The mixture was stirred at 65°C for 5 h, followed by the treatment with water and ethyl acetate. The organic layer was separated, washed with water and dried over magnesium sulphate. After removing the solvent, the residue was purified by colomn chromatography to yield the tetrahydropyranyl ester. The ester (1·20 g) was dissolved in 10 ml of ethanol containing *p*-toluenesulphonic acid and heated, followed by dilution with water. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and dried over magnesium sulphate. The removal of the solvent left a crystalline mass in a 90 per cent yield. ^{1}H NMR (CDCl$_3$) δ (ppm): 0·9 (t, 3 H, CH$_3$), 1·0–2·15 (m, 24 H, CH$_2$), 2·35 (t, 2 H, CH$_2$ COO), 3·8–4·2 (m, 4 H, OCH$_2$), 6·3–6·7 (m, 2 H, Ar–H), 7·8 (d, 1 H, Ar–H), 10·3 (s, 1 H, CHO), 11·5 (s, 1 H, COOH).

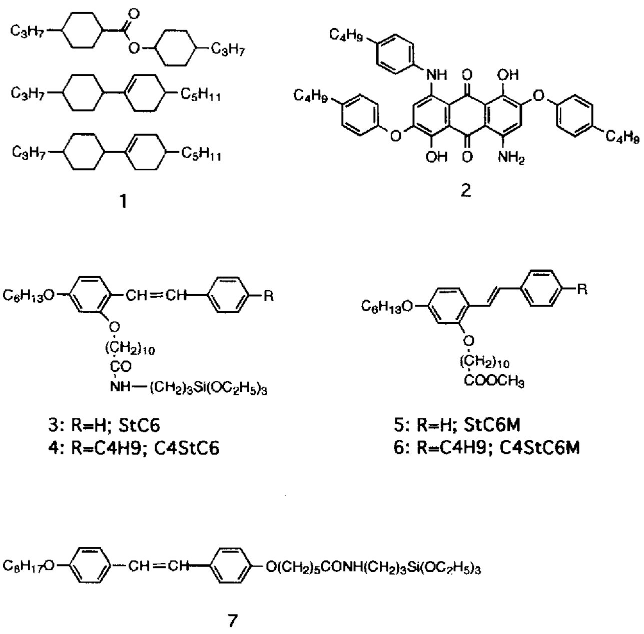

Figure 1. Chemical structures of the nematic liquid crystal (**1**), dichroic dye (**2**), side-on type stilbene silylating reagents (**3** and **4**), stilbene esters (**5** and **6**) and a head-on type stilbene silylating reagent (**7**).

2.2.3. *Methyl 11-(2-formyl-5-hexyloxyphenoxy)undecanoate*

A solution of 11-(2-formyl-5-hexyloxyphenoxy)undecanoic acid (0·83 g) in 5 ml of dichloromethane containing a drop of DMF was heated at reflux for 30 min in the presence of 0·27 ml oxalyl chloride, and then evaporated to dryness. The dichloromethane solution of the residue was added to a 10 ml solution of methanol containing 0·23 g triethylamine and washed with water. The dichloromethane solution was dried over magnesium sulphate and evaporated to dryness. The residual oil was subjected to column chromatography on silica gel to isolate the methyl ester in an 86 per cent yield. ^{1}H NMR (CDCl$_3$) δ (ppm): 0·9 (t, 3 H, CH$_3$), 1·0–2·1 (m, 24 H, CH$_3$), 2·3 (t, 2 H, CH$_2$COO), 3·65 (s, 3 H, COOCH$_3$), 3·8–4·2 (m, 4 H, OCH$_2$), 6·3–6·7 (m, 2 H, Ar–H), 7·8 (d, 1 H, Ar–H), 10·3 (s, 1 H, CHO).

2.2.4. *Methyl 11-[2-(2-phenylethenyl)-5-hexyloxyphenoxy]undecanoate (5)*

After addition of 1·61 M *n*-butyllithium in hexane (1·24 ml) to a suspension of 0·90 g benzyltriphenylphosphonium chloride in 20 ml diethyl ether, a solution of methyl 11-(2-formyl-5-hexyloxyphenoxy)undecanoate (0·074 g) in 10 ml of anhydrous ether was added dropwise to the ylide solution at 0°C and stirred for 30 min at 0°C, followed by stirring for 1 h at room temperature, under an argon atmosphere. The mixture was washed with water, and the ether layer dried over magnesium sulphate. Following the removal of the solvent under a reduced pressure, the residue was purified by column chromatography on silica gel with a 1 : 1 (v/v) mixture of chloroform and hexane to give the stilbene ester as a colourless oil in a 32 per cent yield. ^{1}H NMR (CDCl$_3$) δ (ppm): 0·9 (t, 3 H, CH$_3$), 1·0–2·1 (m, 24 H, CH$_3$), 2·3 (t, 2 H, CH$_2$COO), 3·65 (s, 3 H, COOCH$_3$), 3·7–4·1 (m, 4 H, OCH$_2$), 6·0–7·6 (m, 10 H, Ar–H). Elemental analysis—Found: C, 77·69; H, 9·37 per cent. Calculated for C$_{32}$H$_{46}$O$_4$: C, 77·06; H, 9·47 per cent. HPLC analysis revealed that the stilbene ester is a mixture of the *E* and the *Z* isomers in a 58:42 ratio.

2.2.5. *11-[2-(2-Phenylethenyl)-5-hexyloxyphenoxy]undecanoic acid*

The corresponding ester (0·35 g) was dissolved in 3 ml of methanol with 0·12 g potassium hydroxide. The solution was stirred at 50°C for 30 min and treated with water and dichloromethane. The organic layer was washed with water and dried, followed by the removal of the solvent under reduced pressure to give a colourless crystalline mass in a 90 per cent yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0·9 (t, 3 H, CH_3), 1·0–2·1 (m, 24 H, CH_2), 2·3 (t, 2 H, CH_2COO), 3·7–4·1 (m, 4 H, OCH_2), 6·0–7·6 (m, 10 H, CH=CH and Ar–H).

2.2.6. *N-(3-Triethoxysilyl)propyl-11-[2-(2-phenylethenyl)-5-hexyloxyphenoxy]undecanamide (3)*

To a solution of the corresponding carboxylic acid (0·15 g) and 3-aminopropyltriethoxysilane (0·08 g) in 2 ml of DMF was added diphenyl phosphorylazide (0·12 g) in 2 ml of DMF. Triethylamine (0·04 g) in 2 ml of DMF was added dropwise to the solution at 0°C, and the mixture stirred for 2 h at 0°C, followed by overnight at room temperature. The solution was mixed with hexane, washed with chilled water and dried over magnesium sulphate. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a 1 : 1 mixture of hexane and ethyl acetate to give the silylating reagent as a colourless paste in a 33 per cent yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0·6 (t, 2 H, CH_2Si), 0·9 (t, 3 H, CH_3), 1·0–2·0 (m, 35 H, CH_3 and CH_2), 2·15 (t, 2 H, CH_2CO), 3·0–3·4 (m, 2 H, $NHCH_2$), 3·5–4·1 (m, 10 H, CH_2O), 5·7 (s, 1 H, NH), 6·0–7·6 (m, 10 H, CH=CH and Ar–H).

2.2.7. *2-Hydroxy-4-hexyloxy-4′-butylstilbene*

After the addition of 1·61 M *n*-butyllithium in hexane (6·00 ml) to a suspension of 4·84 g 4-butylbenzyltriphenylphosphonium bromide in 50 ml of anhydrous diethyl ether, a solution of 2-hydroxy-4-hexyloxybenzaldehyde (1·00 g) in 10 ml of anhydrous ether was added dropwise to the solution, followed by heating at reflux for 15 min. The reaction mixture was treated with diluted hydrochloric acid and washed with water to separate the organic layer. After drying over magnesium sulphate, the solvent was removed to leave a residue. This was purified by column chromatography on silica gel using a 1 : 1 mixture of chloroform and hexane to afford colourless crystals of m.p. 60–64°C in a 90 per cent yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0·9 (t, 6 H, CH_3), 1·1–2·0 (m, 12 H, CH_2), 2·6 (t, 2 H, Ar–H), 3·9 (t, 2 H, OCH_2), 5·1 (s, 1 H, OH), 6·2–7·6 (m, 9 H, CH=CH and Ar–H). Elemental analysis—Found: C, 81·18; H, 9·27 per cent. Calculated for $C_{24}H_{32}O_2$: C, 81·77; H, 9·15 per cent.

2.2.8. *11-[2-(2-(4-Butylphenyl)ethnyl)-5-hexyloxyphenoxy]undecanoic acid*

A solution of 2-hydroxy-4-hexyloxy-4′-butylstilbene (1·46 g) and tetrahydropyranyl 11-bromoundecanoate (1·59 g) in 7 ml of DMF was stirred at 65°C for 3 h in the presence of 0·63 g potassium carbonate. The mixture was diluted with benzene, washed with water and dried over magnesium sulphate. After the removal of the solvent, the residual oil was purified by column chromatography on silica gel using a 19 : 1 (v/v) mixture of hexane and ethyl acetate to give the stilbene tetrahydropyranylester as a colourless oil in a 67 per cent yield. The ester (0·80 g) was dissolved in a 9 : 1 mixture of ethanol and hexane containing *p*-toluenesulphonic acid. The solution was stirred for 2 h at room temperature, washed with water and dried. Evaporation of the solvent gave the stilbene carboxylic acid as a paste in a 90 per cent yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0·9 (t, 6 H, CH_3), 1·0–2·1 (m, 28 H, CH_2), 2·3 (t, 2 H, CH_2COO), 2·6 (t, 2 H, Ar–CH_2), 3·7–4·1 (m, 4 H, OCH_2), 6·3–7·6 (m, 9 H, CH=CH and Ar–H), 10·2 (s, 1 H, COOH). IR (neat): 2930, 2850, 1720, 1600 cm^{-1}.

The carboxylic acid was converted into the methyl ester (**6**) through the corresponding acid chloride.

2.2.9. *N-(3-Triethoxysilyl)propyl-11-[2-(2-(4-butylphenyl)ethenyl)-5-(hexyloxy)phenoxy]undecanamide (4)*

To a solution of the corresponding stilbene carboxylic acid (0·20 g) and 3-aminopropyltriethoxysilane (0·09 g) in 2 ml of DMF was added diphenyl phosphorylazide (0·11 g) in 2 ml of DMF. Triethylamine (0·04 g) in 2 ml DMF was added dropwise to the solution at 0°C, and the mixture was stirred for 2 h at 0°C, followed by overnight at room temperature. The solution was mixed with hexane, washed with chilled water and dried over magnesium sulphate. After removing the solvent, the residue was purified by means of column chromatography on silica gel using a 1 : 1 mixture of hexane and ethyl acetate to give the silylating reagent as a colourless paste in a 62 per cent yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0·6 (t, 2 H, CH_2Si), 0·9 (t, 6 H, CH_3), 1·0–2·0 (m, 37 H, CH_2 and CH_3), 2·2 (t, 2 H, CH_2CO), 2·6 (t, 2 H, Ar–H), 3·0–3·4 (m, 2 H, $NHCH_2$), 3·5–4·1 (m, 10 H, CH_2O), 5·7 (s, 1 H, NH), 6·3–7·6 (m, 9 H, CH=CH and Ar–H).

2.2. *Surface modification and cell fabrication*

A quartz plate (1 × 3 cm^2) was cleansed ultrasonically in acetone, deionized water, 12 M nitric acid, a 5 wt % aqueous solution of sodium bicarbonate and deionized water for 10 min each, followed by drying at 100°C for

30 min. The plate was immersed in a 1 wt % solution of a stilbene silylating reagent in 1 : 1 w/w mixture of benzene and ethanol for 30 min. The plate was baked at 100°C for 30 min and subjected to the repeated ultrasonic treatment in benzene for 10 min.

A nematic LC (EXP-CIL), a ternary mixture of a cyclohexyl cyclohexanecarboxylate and two cyclohexylcyclohexenes (see figure 1), was put between the stilbene-modified plate and a quartz plate treated with lecithin for homeotropic alignment to make a hybrid cell. The cell thickness was adjusted by spherical spacers of a diameter of 5 μm suspended in the LC.

2.3. *Photoirradiation*

The photodegradation of stilbenes on a quartz surface was carried out with a 500 W high pressure mercury arc without a filter. The irradiation of the solution and the cell with monochromatic light was achieved with a JASCO Spectro Irradiator equipped with a 1 kW xenon lamp. Light intensity was monitored by the chemical actinometry of a fulgide.

2.4. *Photoalignment determination*

The procedures for photoirradiation and photobirefringence measurement of the LC cell were performed in the same manner as reported in our previous papers. Figure 2 shows the polarization angle (θ) between the electric vector of actinic light and the cell axis, and the probing light angle (ϕ) between the electric vector of the polarized He–Ne laser reference beam and the cell axis.

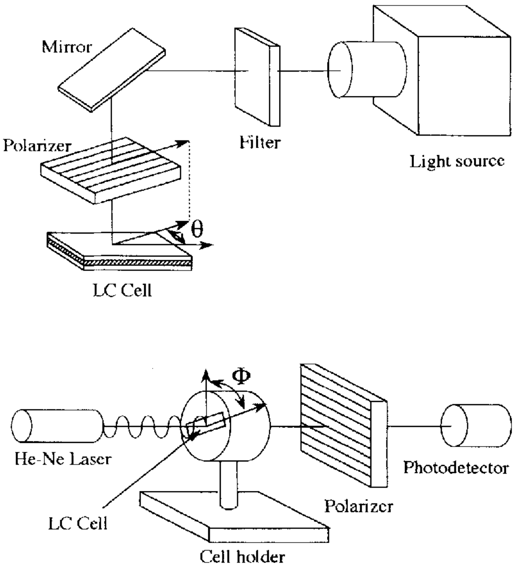

Figure 2. Polarization plane angles of the actinic light (θ) and probe light (ϕ).

2.5. *Photoisomerization in solution*

An acetonitrile solution of the stilbene ester (**5** or **6**) ($10^{-2} \sim 10^{-3}$ mol l^{-1}) placed in a quartz cell of 1 mm thickness was irradiated with UV light until no marked alteration of the electronic absorption spectra was detected due to the formation of a photostationary state. An irradiated solution was subjected to HPLC with a reverse phase column, a JASCO Finepak SIL, using acetonitrile as eluent at a flow rate of 0·5–1·0 ml min^{-1}. The isomers were monitored by measuring absorbances at an isosbestic wavelength during the photoisomerization using a Union Giken MCPC-350. An isomeric ratio was calculated from the peak areas.

2.6. *Physical measurements*

Electronic absorption spectra were taken on a Hitachi 320 spectrophotometer or a Hewlett Packard 8452A diode array spectrophotometer. NMR and IR measurements were performed with the use of a JEOL FX90Q and JEOL JIR-3505, respectively. Fluorescent spectra were obtained with aid of a Hitachi F4000. Atomic force microscopy was measured with a Seiko Instrument SFA300.

3. Results

3.1. *Synthesis and photochemistry*

Figure 1 shows the structure of the stilbenes (**3** and **4**) having triethoxysilyl moiety in the *o*-position. Because of the difference in the synthetic routes, the stilbene (**3**: StC6) having a hexyloxy group at one of the *p*-positions was a 42 : 58 mixture of the *E*- and *Z*-isomers while the other stilbene (**4**: C4StC6) substituted with both butyl and hexyloxy groups was the pure *E*-isomer. Both silylating reagents were purified by column chromatography on silica gel for the surface modification of quartz plates. The average area occupied by each olefinic chromophore on the quartz surface was estimated by UV absorption assuming that the absorption coefficients of the chromophores were not affected by the surface attachment. The surface occupied areas of C4StC6 and StC6 were 0·93 nm^2 and 0·85 nm^2 per molecule, respectively.

The photochemical reaction of stilbenes involves two processes; the *E*/*Z*-isomerization and the 6π-electrocyclization of the *Z*-isomer to phenanthrenes [14]. The photochemistry was confirmed by irradiating an ethanol solution of the stilbene methyl ester (**5**) instead of **3** and **4** because the latter are labile owing to the presence of hydrolysable triethylsilyl residue. Figure 3 shows the spectral changes of **5** upon irradiation with UV (> 330 nm) light. Under the present UV irradiation conditions, the solution reached a photostationary state within a few seconds, followed by the gradual formation of a phenanthrene upon prolonged irradi-

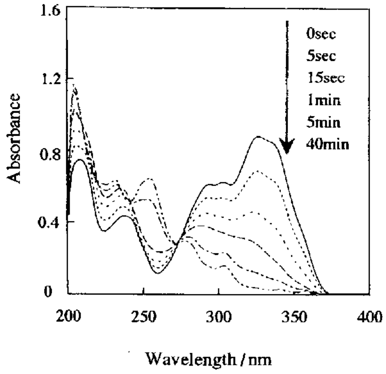

Figure 3. Spectral changes of the stilbene ester (**5**) in ethanol during UV irradiation.

ation. Table 1 shows the isomer ratios of both stilbenes in photostationary states upon UV irradiation with light of variant wavelengths.

The successive reaction mode from the starting compound (*E*-isomer) to the product (phenanthrene) through an intermediate (*E*-isomer) upon prolonged UV irradiation was confirmed conveniently by the spectral analysis with the extinction coefficient difference quotient (EDQ) diagram which gave a linear relationship [15]. The formation of a phenanthrene in the UV-exposed solution was checked by measuring fluorescence and excitation spectra. A fluorescence spectrum of the UV irradiated solution had emission maxima at 366, 389 and 403 nm whereas the maxima in an excitation spectrum appeared at 253, 278 and 303 nm, respectively. These maxima were red-shifted when compared with the parent phenanthrene due to the substitution with alkoxy groups. The maxima in the excitation spectra were identical to those in the corresponding absorption spectra, supporting the formation of phenanthrene moiety by the oxidative cyclization upon prolonged irradiation.

The UV exposure of plates surface-modified with the stilbenes caused a spectral change quite similar to that in solution; the rapid photoisomerization and the subsequent gradual photodegradation of the stilbene moiety (see figure 4). The estimation of the *E*/*Z* ratio in a photostationary state on the surface failed because of the very low absorbances in their electronic absorption spectra. However, the formation of a phenanthrene after prolonged UV irradiation on the surface was detected by fluorescence measurement.

Table 1. The wavelength dependence of the isomer ratio of the stilbenes in photostationary states.

		trans	*cis*
Stilbene	Irradiation wavelength/nm	/per cent	
StC6M	Before irradiation	42	58
	260	52	48
	290	34	66
	330	26	74
C4StC6M	Before irradiation	100	0
	260	77	23
	290	45	55
	330	27	73

3.2. *Photoalignment*

A hybrid cell was assembled by sandwiching the LC (EXP-CIL) (**1**) between a quartz plate surface-modified with a stilbene and a plate treated with lecithin for homeotropic alignment and exposed to polarized UV light with an irradiation angle (θ) (see figure 2) [1, 3, 4]. The photoinduced alignment was monitored by following the transmittance of a polarized probing He–Ne laser light as a function of a rotational angle (ϕ) of the cell during the polarized light irradiation at intervals to evaluate the photoinduced birefringence. Irradiation was performed at room temperature until no essential alteration of the UV absorption spectra was observed. Figure 5 shows the results for the alignment of the LC in a cell (C4StC6-cell) made from a plate modified with the C4StC6 silylating reagent (**4**) upon exposure to polarized

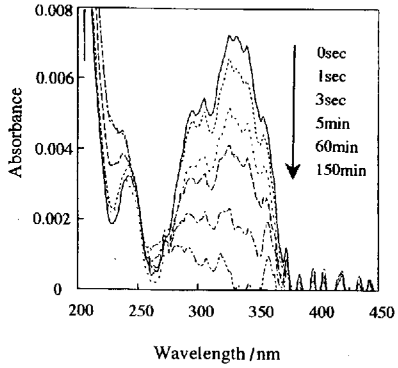

Figure 4. Spectral changes of the quartz plate modified with the C4StC6 silylating reagent (**4**).

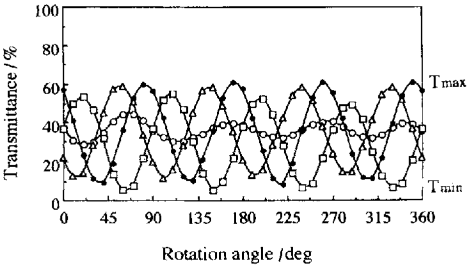

Figure 5. Photoinduced reorientation of an EXP-CIL filled surface-modified with C4StC6 before (○) and after subsequent irradiation with polarized 260 nm light at $\theta=90°$ of exposure energy of 0·21 J cm^{-2} (△), $\theta=45°$ of 0·53 J cm^{-2} (□) and $\theta=20°$ of 0·42 J cm^{-2} (●).

260 nm light at $\theta = 90°$, 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 $\sin^2(2\phi)$. This means that a uniaxial alignment was induced by polarized light irradiation even at room temperature. The orientational direction of the photoinduced homogeneous alignment was determined by the measurement of the dichroism of a dichroic anthraquinone dye (**2** in figure 1) dissolved in the LC layer. The result is indicated in figure 6. Since dye molecules align parallel to rod-like mesogenic molecules and the transition moment of the dye is parallel to the molecular axis, the direction of the mesophase orientation is confirmed to be approximately perpendicular to the electric vector of the actinic light.

One of the characteristics of the surface-assisted photoalignment regulation involves the rewritability of photoimages; the direction of the homogeneous alignment can be controlled reversibly by changing the electric vector of actinic light when the cell surfaces are modified with azobenzenes [1, 3, 4] or a spiropyrane [10]. This was confirmed by successive irradiation with 260 nm polarized light after rotating the polarization plane axis at $\theta = 45°$ and 20°, respectively. The results for the cell modified with C4StC6 are shown in figure 5 as a typical example. The regular patterns demonstrate a parallel shift, indicating that the alignment direction is determined by a polarization plane angle.

The wavelength effect on the photoalignment was studied by illuminating cells with polarized light of various wavelengths. Each cell was irradiated first with light of $\theta = 0°$ for the initial induction of the homogeneous alignment until no marked alteration was detected in the alignment. Subsequently, the cell was illuminated after setting the polarization plane of actinic light at $\theta = 45°$. During the irradiation, the alignment direction was estimated at intervals by monitoring the transmittance of the probing polarized light as a function of the rotational angle (ϕ) of the cells. The alignment direction was gradually rotated with slight modification of the transmittance curve, reflecting the deterioration of the photobirefringence during the reorientation. After the exposure of the cell to the light of an energy great enough to result in the completion of the subsequent alignment, the polarization plane was switched again to $\theta = 70°$ to give rise to the third reorientation. The results are compiled in table 2. Here, $\Delta\theta$ and $\Delta\phi$ denote the differences in the polarization plane angle of the actinic light and in the alignment direction between the initial and the subsequent irradiation, respectively. They correspond to the measure of an immature reorientation.

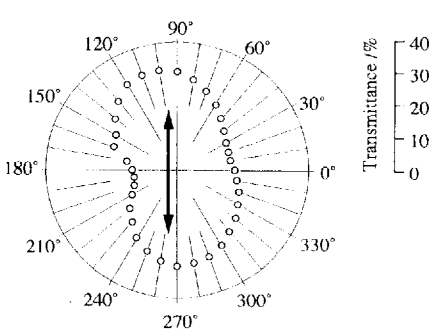

Figure 6. Photoinduced dichroism of a cell filled with EXP-CIL doped with the anthraquinone dye (**2**) after LPL irradiation at 260 nm. The arrow shows the direction of the electric vector of the polarized actinic light.

Polarized microscopic observation of the cell after the LPL irradiation showed that the mesophase layer contained optical defects owing to disclination lines and a partially incomplete uniaxial alignment. These optical defects caused a leakage of monitoring light at the crossed position of the cell to increase the minimum transmittance. Thus, the contrast defined as $T_{\max}/T_{\min}$, where $T_{\max}$ and $T_{\min}$ stand for the maximum and minimum transmittances of the probing light, respectively, is assumed to be a qualitative measure for the evaluation of the optical quality of the photoirradiated cell. Calculated contrast values are also summarized in table 2. The irradiation with 330 nm light gives rise to poorer contrast values for both cells while the 260 nm irradiation is more favourable for a homogeneous alignment.

4. Discussion

A previous paper described that the surface modification of a quartz plate with the stilbene (**7**) substituted with an octyloxy group in the *p*-position (head-on type attachment) brings about a homeotropic alignment of the nematic LC when the chromophore is attached to the surface in the *p*′-position [16]. The alternate irradiation with UV light in different wavelength regions gave a reversible alignment change between homeotropic and planar modes. Since the present work aims at an in-plane alignment photocontrol, a substrate surface covered with stilbene should give rise to a planar mode. As discussed in our recent papers [1, 4], the linkage of azobenzene moieties on a substrate surface in their *o*-position referred to as the side-on type attachment provides favourably a planar alignment to fulfill one of the requirements for the in-plane photoalignment regulation.

The reason for using the nematic LC, EXP-CIL, as a ternary mixture of one cyclohexyl cyclohexanecarboxylate and two cyclohexylcyclohexenes in this work is twofold. First, this LC is highly transparent to UV light for the olefine photoisomerizations so that undesirable photodegradation of the mesophase can be minimized. Second, the transition temperature between the nematic and isotropic phases (T_{NI}) at 31·5° is close to room

Table 2. Photoalignment direction (ϕ) as a function of the direction (θ) of the electric vector of polarized light at various wavelengths.

	Polarized light			Aligned direction[b]			
Stilbene	Wavelength/nm	Exposure energy[a]/J cm^{-2}	Plane angle θ/°	$\Delta\theta$	$\Delta\phi$	δ	Contrast[c]
St0C6	260	0·17	0	–	–		5·1 ± 1·1
		0·51	45	45	44	1	5·6 ± 0·5
	290	1·8	0	–	–		3·5 ± 0·5
		3·2	45	45	32	13	6·9 ± 1·3
		2·0	70	70	42	28	7·5 ± 1·5
	330	1·7	0	–	–		3·2 ± 0·5
		3·4	45	45	10	35	3·9 ± 0·9
		3·4	70	70	18	52	3·3 ± 0·5
C4St0C6	260	0·21	0	–	–		6·1 ± 0·7
		0·53	45	45	39	6	9·5 ± 1·2
		0·42	70	70	65	5	6·8 ± 1·0
	290	0·094	0	–	–		3·2 ± 0·5
		0·58	45	45	45	0	6·6 ± 0·2
		0·83	70	70	68	2	5·8 ± 0·5
	330	1·7	0	–	–		2·3 ± 0·4
		10·0	45	45	35	10	3·8 ± 0·4
		6·8	70	70	49	21	4·3 ± 0·7

[a] Exposed energy required to reorient EXP-CIL.
[b] Within ± 2° error.
[c] T_{max}/T_{min} (see figure 5).

temperature. As revealed in our work, the surface-assisted photoalignment of nematic LCs is influenced markedly by the cell temperature during LPL irradiation [1, 4]. The photoinduced reorientation of mesogenic molecules is dramatically enhanced at temperatures close to or above T_{NI}. The low T_{NI} enabled us to carry out the photoalignment experiment at room temperature.

The azimuthal direction of the photoalignment was perpendicular to the electric vector of actinic light. This is in line with the results for LC cells surface-modified with azobenzene chromophores [1, 3, 4]. Just as in the case of azobenzenes, the transition moment of stilbene lies parallel to the longitudinal axis of the molecule so that the rearrangement of the chromophore takes place to give the perpendicular reorientation as a result of the repetition of the geometrical photoisomerization.

Table 2 shows that the photoalignment efficiency is influenced by the excitation wavelength. The exposure energy required for the LC reorientation is largest for 330 nm light. As indicated in table 1, the 330 nm light irradiation results favourably in a predominant formation of the *Z*-isomer whereas the amount of the *Z*-isomer is reduced upon irradiation with the light of shorter wavelengths at 260 nm and 290 nm. The results summarized in table 2 can be reasonably interpreted by the assumption that the alignment of LC molecules arises from the perpendicular reorientation of the *E*-stilbene units on the surface by the action of polarized light. This is closely related to the photocontrol by surface azobenzenes. In our previous papers on the in-plane alignment photocontrol of LCs by side-on type azobenzenes on a substrate surface, irradiation with polarized blue light leads to perpendicular reorientation which is caused by uniaxial arrangement of the surface azobenzenes [1, 4]. In the azobenzene case, the photostationary state under blue light illumination contains the *E*-isomer as the major component which is favourable for the in-plane alignment control. Thus, both stilbenes and azobenzenes at topmost surfaces trigger the in-plane reorientation of a nematic mesophase when the rod-like *E*-isomer is major under the illumination condition. The critical role of the *E*-isomer was also confirmed by the wavelength effect on the contrast of photoaligned states; 330 nm light irradiation leading to a minor amount of the *E*-isomer gives rise to a poorer contrast.

Table 2 tells us furthermore that the effect of the butyl group on the stilbene moiety is twofold. First, the presence of the *p*-butyl group in C4StC6 leads to the reduction of both the exposure energy for the reorientation and the delay of reorientation direction (δ). This is in particular prominent when the irradiation is made with 290 nm light. These imply that the butyl group plays a certain role in triggering the reorientation of LC molecules possibly because of the mimicking effect of the mesogenic structure.

As stated above, the direction of the photoinduced alignment is approximately perpendicular to the electric vector of the polarized light plane. If this situation takes place in all cases, $\Delta\theta$ should be equal to $\Delta\phi$. As table 2 shows, this relation does not always hold true, in particular depending on the irradiation wavelength and the structure of the stilbene. Here, δ is defined as a delay in the reorientation direction of the LC and equal to the difference between $\Delta\theta$ and $\Delta\phi$. Thus, if $\delta = 0$, the perpendicular reorientation should be complete upon subsequent irradiation with light of a different polarization plane. The δ value is zero within experimental error 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. On the contrary, δ becomes much larger under illumination with light of wavelengths at 290 nm and 330 nm, respectively. A similar trend was observed for a cell surface-modified with C4StC6 though the values are much smaller.

It is noteworthy that the photoinduced LC reorientation is achieved in some cases upon prolonged photoirradiation of energies of no more than a few J cm^{-2} [2, 12]. As mentioned above, the irradiation of the stilbenes for longer times results in photodegradation leading to the oxidative cyclization to phenanthrenes (see figure 4). This implies that the commanding ability discussed so far is not always due to the stilbenes, but also due to phenanthrenes which cannot display the photoisomerizability any longer. In order to check the possibility that the phenanthrene moiety on a surface acts as a commander molecule for the in-plane alignment photocontrol, the plate modified with the stilbene was previously irradiated with polarized light at 290 nm to convert it into a phenanthrene, followed by the assemblage of the LC cell. No photoalignment was observed at all. Subsequent irradiation of the cell with polarized 290 nm light also caused no homogeneous alignment. Such a negative result does not always eliminate the possibility that the phenanthrene moiety can be reoriented on a substrate surface by polarized light to bring about a homogeneous alignment. It has been revealed that the photoinduced uniaxial orientation of azobenzene units on a surface is considerably stabilized by the presence of LC molecules while the surface dichroism of the azochromophoric groups fades away when the surface is not in contact with a mesogenic layer [17]. This implies that the reorientational behaviour of photoactive molecules localized at a topmost surface is dramatically influenced by the presence of LC molecules owing to a cooperative work. Further studies are needed on the possibility to photocontrol of the azimuthal alignment of LCs by non-photoisomerizable units through photophysical processes.

5. Conclusions

Stilbenes exhibiting the geometrical photoisomerization can trigger the in-plane reorientation of a nematic LC of a low T_{NI} upon polarized irradiation at room temperature when the chromophores are covalently bound on a silica surface through a polymethylene spacer. The efficiency of the photoalignment control is expressed as the contrast (T_{max}/T_{min}) as well as the reorientation angle shift (δ) and influenced considerably by the irradiation wavelength. Better results are obtained by polarized UV light irradiation giving rise to the preferential formation of the *E*-isomer at a photostationary state. This implies that the reorientation of LCs is triggered by the *E*-isomer on the substrate surface. The presence of the butyl group in the *p*-position of the stilbene moiety is also of significance for enhancing the photoalignment efficiency.

Prolonged UV irradiation of the surface chromophores results in side-reactions other than photoisomerization. Despite the disappearance of the major part of olefinic molecules on the surface after prolonged irradiation, the alteration of the polarization plane of actinic light induces the reorientation of the LC layer. The possibility that a phenanthrene, as a photocyclized product, acts as a photoactive unit for the photoalignment is not fully eliminated.

This work was supported by a Grant-in-Aid on Priority-Area-Research 'Photoreaction Dynamics' from the Ministry of Education, Science and Culture.

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