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Hidetoshi Tomita[a]; Kazuaki Kudo[a]; Kunihiro Ichimura[a]
[a] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Yokohama, Japan

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Command surfaces 15 [1]. Photoregulation of liquid crystal alignment by cinnamoyl residues on a silica surface

by HIDETOSHI TOMITA, KAZUAKI KUDO and KUNIHIRO ICHIMURA*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

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The surface of a silica substrate plate was modified with a cinnamate moiety having a triethoxysilyl group at the *ortho*-position through a spacer. The plate was employed to assemble a cell filled with a nematic liquid crystal and exposed to linearly polarized 259 nm light to obtain homogeneous alignment. The direction of the alignment was perpendicular to an electric vector of the actinic light. On the contrary, the exposure of the cell to polarized light at 330 nm did not result in homogeneous alignment while the actinic light caused the disappearance of the chromophore. This wavelength effect on the azimuthal photoalignment suggests that the surface-assisted liquid crystal orientation is triggered by the reorientation of the *E*-isomer of the cinnamate group. This is in marked contrast to a proposed mechanism of a photoalignment by a thin film of a poly(vinyl cinnamate) derivative (Schadt *et al.*, 1993, *Jpn J. appl. Phys.*, **31**, 2155); homogeneous alignment is induced by the axially selective photodimerization of cinnamate groups.

1. Introduction

Uniaxial alignment of nematic liquid crystals (LCs) is induced by the molecular structural alteration of photoisomerizable moieties attached to a substrate surface termed a command surface upon irradiation with linearly polarized light [1–10]. Such a surface-assisted photocontrol of the in-plane LC alignment has been achieved by modifying the topmost surface of a substrate plate with photochromic molecules, for example, azobenzenes [4–10] and a spiropyran [11]. Recent reports have described that a thin film of poly(vinyl cinnamates), one of the representative photocrosslinkable photoresists, providing a photoactive surface to achieve the in-plane alignment photocontrol with polarized UV light irradiation [12, 13]. This technique is of practical significance since an LC aligning film, which is a key material in constructing conventional LC displays, becomes available photochemically without any mechanical treatment of a thin film of polymer like a polyimide [14]. The alignment mechanism of the photocrosslinkable polymers has been proposed as follows; exposure of a film to polarized UV light results in the axial-selective crosslinking reaction involving the cyclobutane formation which determines the uniaxial orientation of LC molecules [12].

In our preceding paper [1], a silica surface modified with stilbenes acts as a command surface to control the in-plane alignment of a nematic LC by linearly polarized UV light. The alignment of photocontrol is based on the geometrical photoisomerization around the carbon–carbon double bond. Cinnamates are similar to azobenzenes and stilbenes in the mesogenic structure and the *E*/*Z* photoisomerizability. This work aims at showing that cinnamate moieties on a silica surface are active for photoinduced alignment regulation and suggests that the photoinduced homogeneous alignment is caused by the *E*/*Z* photoisomerization.

2. Experimental

2.1. *Materials*

The nematic liquid crystal, EXP-CIL [1], was kindly supplied by Rodic Co., Ltd and mixed with spherical glass spacers of 5 μm diameter to control the cell gap. A diaminoanthraquinone dye was a gift from Nippon Kayaku Co., Ltd [1].

2.2. *Synthesis*

2.2.1. *Hexyl (E)-2-hydroxy-4-hexyloxycinnamate (3)*

1·00 g 2-hydroxy-4-hexyloxybenzaldehyde (**1**) and 1·90 g hexyl triphenylphosphoranilideneacetate (**2**) in 5 ml benzene was stirred for 1 h at room temperature, followed by washing with water and drying over magnesium sulphate. After removing the solvent, the oily residue was purified by column chromatography on silica gel with a 3:1 (v/v) mixture of hexane and ethyl acetate to give colourless crystals of m.p. 48–54°C in a 90 per cent

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*Author for correspondence.

yield. ^1H NMR ($CDCl_3$) δ (ppm): 0·9 (t, 6 H, CH_3), 1·0–2·0 (m, 16 H, CH_2), 3·95 (t, 2 H, $ArOCH_2$), 4·1–4·4 (m, 2 H, $COOCH_2$), 6·2–6·6 (m, 3 H, CH=C$\underline{H}$COO + Ar–H), 7·4 (d, 1 H, Ar–H), 7·95 (d, 1 H, C$\underline{H}$=CHCOO, $J = 15$ Hz). Elemental analysis—Found: C, 72·38; H, 9·26 per cent. Calculated for $C_{21}H_{32}O_4$: C, 72·26; H, 9·34 per cent.

2.2.2. *(E)-11-[5-Hexyloxy[2-(hexyloxycarbonyl) ethenyl]phenoxy]undecanoic acid*

A solution of 1·00 g hexyl (*E*)-2-hydroxy-4-hexyloxycinnamate and 1·10 g tetrahydropyranyl 11-bromoundecanoate in 5 ml DMF was stirred in the presence of 0·45 g potassium carbonate at 65°C for 3 h. The reaction mixture was diluted with benzene and washed with water, followed by drying and removal of the solvent. The residue was purified by column chromatography on silica gel to give the tetrahydropyranyl ester as an oily residue in a 90 per cent yield. ^1H NMR ($CDCl_3$) δ (ppm): 0·9 (t, 6 H, CH_3), 1·0–2·0 (m, 38 H, CH_2), 2·35 (t, 2 H, CH_2COO), 3·5–4·3 (m, 8 H, OCH_2), 5·95 (m, 1 H, COOCH), 6·2–6·6 (m, 3 H, CH=C$\underline{H}$COO + Ar–H), 7·4 (d, 1 H, Ar–H), 7·95 (d, 1 H, C$\underline{H}$=CHCOO, $J = 15$ Hz).

The ester (1·00 g) was dissolved in 10 ml ethanol containing *p*-toluenesulphonic acid and stirred for 1 h, followed by dilution with dichloromethane. The solution was washed with water, dried over magnesium sulphate, and the solvent removed. The residue was subjected to column chromatography on silica gel to give a colourless crystalline mass in a 90 per cent yield. ^1H NMR ($CDCl_3$) δ (ppm): 0·9 (t, 6 H, CH_3), 1·05–2·0 (m, 32 H, CH_2), 2·35 (t, 2 H, CH_2COO), 3·7–4·3 (m, 6 H, OCH_2), 6·3–6·6 (m, 3 H, CHn2bC$\underline{H}$COO + Ar–H), 7·41 (d, 1 H, Ar–H), 7·9 (d, 1 H, C$\underline{H}$=CHCOO, $J = 15$ Hz), 10·4 (2, 1 H, COOH). IR (neat): 2930, 2850, 1700, 1600 cm^{-1}.

2.2.3. *(E)-N-(3-Triethoxysilylpropyl-11-(5-hexyloxy-2-(2-hexyloxylcarbonylethenyl)phenoxy]undecanamide (4)*

To a solution of 0·20 g of the corresponding carboxamide and 3-aminopropyltriethoxysilane in 2 ml DMF was added 0·12 g of diphenylphosphoryl azide, followed by 0·04 g triethylamine in 2 ml DMF at 0°C. After stirring for 3 h at 0°C, followed by overnight at room temperature. The mixture was diluted with dichloromethane and washed with chilled water, dried over magnesium sulphate and the solvent removed. The residual product was purified by column chromatography on silica gel with a mixture of hexane and ethyl acetate to give a pasty product in a 25 per cent yield. ^1H NMR ($CDCl_3$) δ (ppm): 0·6 (t, 2 H, CH_2Si), 0·9 (t, 6 H, CH_3), 1·0–2·0 (m, 43 H, $CH_2 + CH_3$), 2·15 (t, 2 H, CH_2COO), 3·0–3·4 (m, 2 H, $NHCH_2$), 3·5–4·3 (m, 12 H, OCH_2), 5·85 (s, 1 H, NH), 6·3–6·6 (m, 3 H, CH=C$\underline{H}$COO + Ar–H), 7·4 (d, 1 H, Ar–H), 7·9 (d, 1 H, C$\underline{H}$=CHCOO, $J = 15$ Hz).

2.2. *Surface modification and cell fabrication*

Surface modification with a 1 wt % solution of the cinnamate silylating reagent was performed according to the preceding paper [1]. The nematic LC was put between a plate modified with the cinnamate and a quartz plate treated with lecithin for a homeotropic alignment to make a hybrid cell. A guest–host cell filled with the LC doped with the dichroic dye was assembled in the same way.

2.3. *Photoirradiation*

Irradiation of the solution and cell with monochromatic light was achieved with a JASCO Spectro Irradiation equipped with a 1 kW xenon lamp and monochromator.

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 [4–11].

2.5. *Photoisomerization in solution*

An acetonitrile solution of the cinnamate derivative ($10^{-2} \sim 10^{-3}$ 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. The irradiated solution was subjected to HPLC with a reverse phase column, a JASCO Finepak SIL, using acetonitrile as eluent at a flow rate of 1·0 ml min^{-1}. The isomer composition was monitored by measuring the absorbance at an isosbestic wavelength during the photoisomerization using a Union Giken MCPC-350. An isomeric ratio was calculated from the peak area.

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 JEOL FX90Q and JEOL JIR-35-5, respectively.

3. **Results and discussion**

3.1. *Synthesis and photochemistry*

The molecular design of the cinnamate was made by taking the following into account. First, one of the prerequisites for the photoinduced in-plane alignment regulation of nematic LCs is to make an initial alignment parallel to the substrate surface which is modified with photoactive molecules. As demonstrated in our previous work, a planar orientation is obtained by attaching azobenzenes [10] or silbenes [1] in their *ortho*-position to a silica surface. This type of lateral linkage of photochromic molecules on surfaces has been termed as a side-on type attachment. Second, substitution with alkyl groups to mimick the size and shape of LC molecules is an effective way to improve the commanding ability of the photochromic moieties. Alkyl substituents have been introduced at both *para*-positions of azobenzene [5, 6] as well as stilbene [1] for this purpose. Based on these ideas, a hexyl ester of cinnamate (**4**) was prepared (see figure 1). The benzene ring of the chromophore is substituted with a hexyloxy group in the *para*-position and with a triethoxysilyl residue through a decamethylene spacer in the *ortho*-position. The synthetic route is shown in figure 1. The Wittig reaction of the *o*-hydroxyaldehyde (**1**) with the ylide (**2**) gave exclusively the *trans*-isomer of the cinnamate (**3**) which was carboxyalkylated to give the corresponding carboxylic acid through the ester. The acid was condensed with 3-aminopropyltriethoxysilane to yield the silylating reagent (**4**).

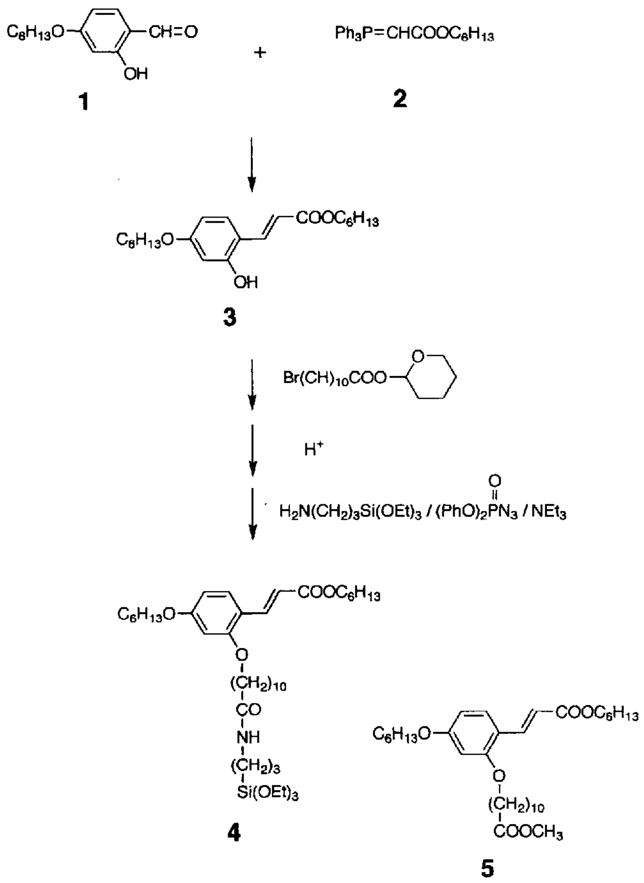

Figure 1. Synthetic route and chemical structures of the cinnamates.

The treatment of a quartz plate with the silyl compound (**4**) was carried out in the conventional way. The average density of the cinnamate groups on the quartz surface was estimated by UV absorption to be 0·93 nm^2 per molecule, assuming that the absorption coefficient of the chromophore did not change on attachment to the surface.

The photoisomerization of the cinnamate was followed by irradiating an ethanol solution of the methyl ester (**5**: $R = OCH_3$) with 330 nm light (see figure 2). The irradiation gave rise to a photostationary state within a few seconds. No spectral alteration was observed even after 1 h irradiation, indicating that no side reaction took place in the dilute solution.

The *E*-to-*Z* isomer ratio in the photostationary state in solution was evaluated by HPLC. Excitation wavelengths were selected on account of the selective light absorption of the *E*-isomer at 330 nm and of the *Z*-isomer at 259 nm. The results are summarized in the table. The *E*-isomer was the major component while the portion of the *Z*-counterpart was larger upon 330 nm irradiation. Because of the overlap of the absorption spectra of both isomers, an exclusive formation of each isomer was not obtained. The photoisomerization on the quartz surface was confirmed spectroscopically. The spectra during the irradiation were so noisy due to very

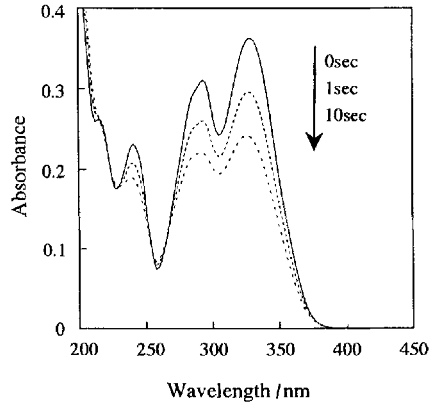

Figure 2. Absorption-spectral changes of the cinnamate (5) in ethanol upon irradiation with >330 nm light.

The photoisomer ratios of the cinnamate (7) in the photo stationary state and the contrast of the cell surface-modified with the cinnamate silylating reagent (5).

Irradiation wavelength/nm	Content of photoisomers/per cent		T_{max}/T_{min}
	trans	*cis*	
259	56	44	13
330	45	55	1·5

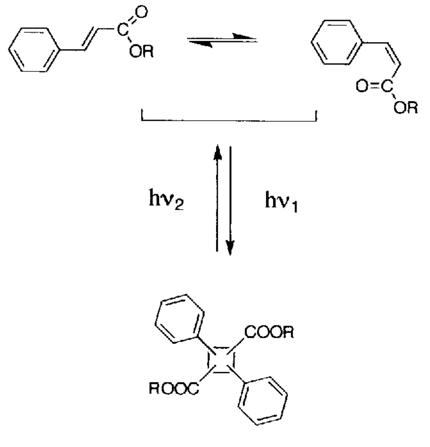

Figure 3. Photochemistry of cinnamates.

small absorbances (less than 0·005) that the estimation of the isomer ratios in the photostationary state on the surface was unsuccessful. Prolonged irradiation with 330 nm light caused a gradual decrease in the absorbances, suggesting the occurrence of side reaction(s) on the quartz plate. From an averaged density of the cinnamate groups on the surface, the average distance between the chromophores was estimated to be *c.* 1 nm. It follows that the possibility of photodimerization on the surface is not eliminated since the cinnamate units are linked to the rigid surface through a relatively long spacer chain. It is well known that cyclobutane as a photodimerized product cleaves to regenerate a couple of the cinnamate groups upon illumination with light at shorter wavelengths which is absorbed by the phenyl rings of the dimer [15] (see figure 3). Thus, a plate exposed to 330 nm light was subsequently irradiated with 259 nm light. A slight increase in the absorption bands was observed. This suggests the regeneration of the cinnamate, implying (2+2) photodimerization on the surface. However, the contribution of the reverse $Z \rightarrow E$ photoisomerization to the spectral modification may play a certain role since the irradiation with 259 nm light is favourable to the formation of the E-isomer in the photostationary state (see the table). Further spectral analysis of the photoproducts is restricted under the present conditions because of the inaccuracy of the absorption spectra so that no distinct conclusions can be made concerning the photodimerization problem. At any rate, it can be said that the 259 nm light irradiation leads to the recovery of the E-isomer.

3.2. *Photoalignment*

UV-transparent EXP-CIL was placed between a quartz plate treated with the cinnamate derivative and a plate treated with lecithin to give a hybrid cell. A low clearing temperature LC ($T_{NI} = 31·8°C$) was used in this work on account of the fact that the photoinduced LC reorientation is enhanced at a temperature close to or above T_{NI} [5]. As described in a previous paper [10], this enabled us to carry out the surface-assisted photoregulation of alignment at room temperature without heating the cell during the polarized photoirradiation.

The cell was first exposed to linearly polarized light at 259 nm. The alignment was monitored according to our conventional manner by measuring the transmittance of light intensity of a polarized probing He–Ne laser beam through the cell and a crossed polarizer placed behind the cell as a function of rotational angle of the cell around the experimental optical axis [4–11]. The mesophase layer exhibited a weak birefringence before the photoirradiation because of the flow-induced alignment of the LC during the cell assembly. Such a phenomenon has been observed frequently in these systems. Polarized irradiation with 259 nm light gave rise to a distinct birefringence formation. Figure 4 shows the results. About 500 mJ cm^{-2} exposure energy was required to obtain homogeneous alignment although polarized microscopy observation showed disclination lines in the aligned texture. The photoaligned cell was subsequently exposed to the polarized light after rotating the electric vector to induce the reorientation of the LC. As can be seen in figure 4, the regular pattern shows a parallel shift, accompanied by a slight shape distortion; the ratios of the transmittances of the peaks ($T_{\max}$) and the valleys ($T_{\min}$) are reduced, indicating that the subsequent irradiation brought about the decrease in the commanding ability of the cinnamate.

The direction of the alignment was confirmed to be perpendicular to the electric vector of the polarized actinic light by measuring the photodichroism of a guest–host cell filled with the LC doped with 0·5 wt %

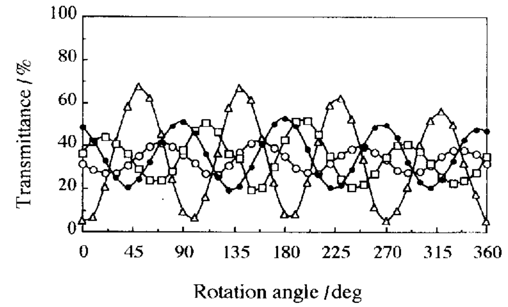

Figure 4. The angular dependence of the transmittance of the monitoring He–Ne laser light though a cinnamate-modified cell filled with EXP-CIL after successive irradiation with linearly polarized 259 nm light. Before irradiation (○), after irradiation at $\theta = 90°$ with an exposure energy of 0·50 J cm^{-2} (△), $\theta = 45°$ of 0·50 J cm^{-2} (□), and $\theta = 20°$ with an energy of 0·57 mJ cm^{-2} (●).

of the dichroic dye (**2**), as presented in figure 5. The result shows unequivocally that the alignment direction of the dye molecules is perpendicular to the electric vector of the polarized light, indicating that the LC orientation is perpendicular to the electric vector of the polarized light.

In a marked contrast to the 259 nm irradiation, no homogeneous alignment was observed with polarized 330 nm light, as shown in figure 6, even though the light induced the *E*/*Z* photoisomerization. No reorientation of the LC molecules was observed at all upon irradiation with the actinic light after rotating the electric vector. There were two possibilities to interprete this unexpected result. First, the LC photoalignment was caused specifically by the absorption of polarized 259 nm light by the LC molecules. We have found recently that a cell surface-modified with benzylideneacetophenone derivatives has no ability to reorient the LC molecules upon irradiation with polarized light and that homogeneous alignment can be induced optically when a cell is filled with LCs which adsorb polarized actinic light [16]. This possibility is discarded in the present case since EXP-CIL is highly UV-transparent and does not absorb 259 nm light. The second possibility is that the irradiation of the cell with 330 nm light results in the preferential photodimerization of the cinnamate on the silica surface to diminish the content of the photoisomerizable units. Since there exists a critical two-dimensional concentration of commander molecules to achieve the photoalignment regulation, the marked reduction of the cinnamate moieties on the surface due to the photodimerization causes the loss of the commanding ability, even though they are photoisomerizable. It is likely that this interpretation is in line with the capability of polarized irradiation with 259 nm light to lead to the photoalignment. As suggested above, the shorter wavelength light leads to the photocleavage of the cyclobutane rings to more or less regenerate the olefinic groups. Such an illumination condition gives rise to a photostationary state between the cinnamates and the cyclobutanes to ensure the repetition of the *E*/*Z* photoisomerization leading to the reorientation of the chromophores.

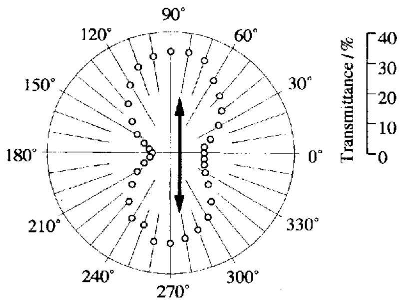

Figure 5. The angular dependence of the transmittance of a linearly polarized He–Ne laser beam through the cinnamate-modified cell filled with EXP-CIL doped with the dichroic anthraquinone dye after exposure to polarized 259 nm light at $\theta = 90°$.

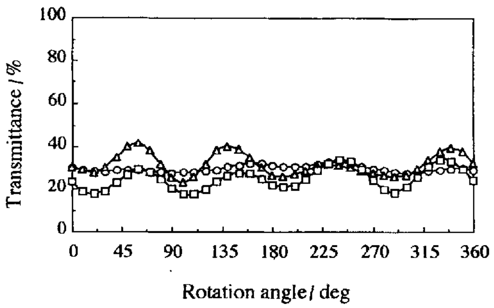

Figure 6. The angular dependence of the transmittance of the monitoring He–Ne laser light through the cinnamate-modified cell filled with EXP-CIL after successive irradiation with linearly polarized 330 nm light. Before irradiation (○), after irradiation at $\theta = 90°$ with a light intensity of 3·6 J cm^{-2} (△), and $\theta = 45°$ with an intensity of 6·7 J cm^{-2} (□).

A novel photoalignment by means of a thin film of photocrosslinkable photoresists, poly(vinyl cinnamates), has been interpreted as a result of the formation of cyclobutanes, the phenyl rings of which determine the direction of the LC homogeneous alignment [12]. Judging from our present results, it is more likely that homogeneous alignment emerges rather not as a result of the cyclobutane formation, but the *E*/*Z* photoisomerization of unreacted cinnamate groups on the uppermost surface of the polymer thin film.

In summary, the photoinduced LC alignment by the cinnamate groups on the silica surface is markedly influenced by the excitation wavelength. Irradiation with linearly polarized 259 nm light results in a reversible reorientation of the UV-transparent nematic LC owing to the *E*/*Z* photoisomerization. The inactiveneess of 330 nm light probably arises from the preference to the (2+2) photoaddition which cannot cause the LC photoalignmenmt.

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