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Reversible alignment change of liquid crystals induced by photochromic molecular films: Properties of azobenzene chromophores covalently attached to silica surfaces

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Reversible alignment change of liquid crystals induced by photochromic molecular films: properties of azobenzene chromophores covalently attached to silica surfaces

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In connection with the mechanism of reversible alignment change of nematic liquid crystals induced by photoisomerizable azobenzene molecules attached to a quartz surface, a static contact angle measurement was carried out for azo-modified plates before and after UV irradiation. The results were not in line with the so-called Friedel–Creagh–Kmetz rule which claims that the alignment is governed by a mutual relationship between a substrate surface energy and surface tension of a liquid crystal. On the other hand, electronic absorption spectra of the plate demonstrated that the ratio of an absorbance at around 340 nm to that at around 240 nm of the azo-chromophore on the surface is reduced by wetting the surface with a UV-transparent nematic liquid crystal. This reflects that the surface azobenzene units are induced to stand approximately perpendicular to the surface upon contact with the liquid crystal. Further discussion is made concerning the photo-induced homogeneous alignment triggered by a rubbed and azo-modified quartz plate determined by polarized absorption spectroscopy.

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1. Introduction

Our previous reports described that the alignment of nematic liquid crystals is regulated by the photoisomerization of azobenzene monolayers attached to substrate surfaces [1] and suggested that this phenomenon is applicable to optical memories and display devices [2]. The procedure to afford such a new type of photo-optical liquid crystal (LC) device, driven by exposure to UV or visible light causing the photoisomerization, involves surface modification of glass plates by silylation with silylating agents having an azobenzene unit [1], by coating a transparent glass plate or a polymer plate with polymer substituted with azobenzene side chains [3] or deposition of Langmuir–Blodgett (LB) films of the polymer [4].

The mechanism of the photoinduced surface-mediated alignment regulation has been proposed as follows, based upon the molecular structure—function relationship. Among the photochromic moieties investigated so far, the photochemical LC alignment regulation has been performed by geometrically photoisomerizable molecules including azobenzene [1–4], stilbene [5] and α-hydrazono-β-ketoester [6] which all possess a common feature: a reversible molecular shape change between the rod-like and the bent forms. This implies that the side by side interactions between the rod-like LC molecules and these photochromic units with similar shape and size attached on to substrate surface is markedly altered by the transformation into the photoisomer with a bent form, leading to the LC alignment modification. In this context, the elucidation of molecular interactions at a boundary region between substrate surfaces and LC molecules is strongly needed in order to make clear the working mechanism of our photoresponsive LC cells.

The LB technique has given us crucial information concerning the molecular interactions at the boundary region because tailored azobenzene molecular films are readily available [4, 7]. Using amphiphilic polymers substituted with *p*-alkylated azobenzene groups to afford

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monolayered, as well as cumulatively layered, LB film, the structure–function relationships, including the effects of average density of the chromophore and spacer length on the photoregulation of nematic LCs, have been elucidated. Molecular films formed by the adsorption of long chain trichlorosilanes upon silica surfaces have been reported to possess ordered structures similar to LB films owing to the collective property based on the van der Waals interaction of alkyl chains [8]. However, surface structures of silica substrates modified with photochromic units should be much more complicated. When trialkoxysilane derivatives are employed to cover substrate surfaces with photochromic units according to one of our conventional techniques to make command surfaces, the structural elucidation of the modified surface becomes tougher since the trialkoxy-type silylating reagents are able to polymerize to form polysiloxanes [9] which may deposit on the substrate surface.

On the one hand, the macroscopic nature of a top-most molecular layer can be described by surface energy which has been discussed in relation to LC alignment modes. In this context, a contact angle measurement for azo-modified plates was achieved revealing the relationship between the photoregularity of LC alignment and contact angles for water on azo-surfaces. On the other hand, azobenzene chromophores can act as probe molecules to elucidate conformations using the ratio of an absorbance due to the transition moment parallel to the molecular long axis to that due to the molecular short axis. This paper deals principally with the relationship between the photoregulation of LC alignment and spectroscopic properties of silica surfaces modified with azobenzenes by silylation. This type of study may afford an alternative approach to understanding structures of amorphous solid surfaces at a molecular level.

2. Experimental

2.1. *Materials*

Liquid crystals (DON-103, DON-602, RO-571 and EXP-CIL) were kindly donated by Rodic Co., Ltd. and summarized in figure 1. Others (K-24 and MBBA) were commercially available and used without further purification. Ethyltriethoxysilane (ETS), 3-aminopropyltriethoxysilane (ATS) and 3-aminopropyldimethylethoxysilane (ADS) were all distilled before use. Silylating reagents incorporating the azobenzene moiety were prepared by the condensation of an azobenzene-carboxylic acid with the corresponding aminopropysilane with use of dicyclohexylcarbodiimide according to our previous paper [1] and used for surface treatment without further purification.

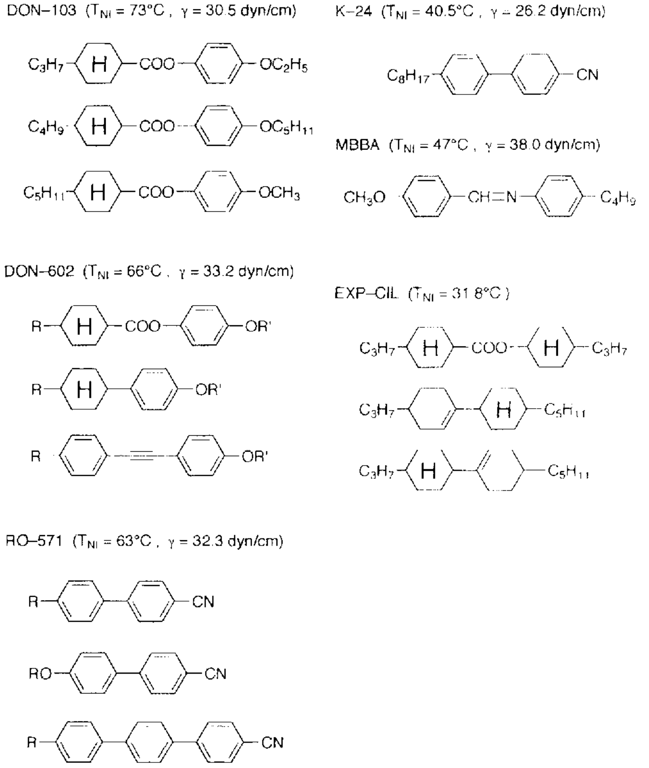

Figure 1. Chemical structures of the LCs.

2.2. *Surface silylation*

Cleansed quartz plates ($1 \times 3\,cm^2$) were immersed in an ethanol solution of a *c*. 1 wt% silylating reagent for 15 min, heated at 120°C for 20 min, washed ultrasonically in dichloromethane and finally dried at 120°C.

2.3. *Physical measurements*

Electronic absorption spectra were taken on a Shimadzu UV-160 spectrophotometer. Dichroic absorption measurements were made on the spectrophotometer using a Glan–Thomson prism set in front of a sample plate. Static contact angle measurements were performed with the aid of a Kyowa Scientific Co. CA-P contact angle meter, at an ambient temperature. Contact angles were measured in 30 s after putting a water droplet of an azo-modified plate ($2{\cdot}7 \times 7{\cdot}0\,cm^2$). An azo-modified plate was exposed to UV light form a 500 W high pressure mercury arc through a band pass filter for 365 nm light and subjected to the contact angle measurement by putting a water droplet three times on fresh areas of the plate. The plate was then irradiated with visible light of >430 nm through a cut-off filter, and contact angles were measured in the same way. This procedure was repeated. Each experiment was performed three times to give mean values with an experimental error of *c*. ± 1·0°). For Zisman plot measurements, a droplet of reference liquid was put on a plate surface-modified with *p*-hexylazobenzene. The

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plate was cleaned in acetone ultrasonically and dried at 120°C for 30 min before the measurement. The reference liquids used were water, formamide, diiodomethane, 1-bromonaphthalene, tricresylphosphate, benzonitrile and heptyloxybenzaldehyde. The contact angle measurements were performed three times to give mean values. The same plate was washed with acetone ultrasonically and dried 120°C for 30 min, followed by irradiation with visible light of >430 nm. The contact angles for the reference solvents were measured three times in the same manner. Experimental errors were within *c.* 2·0°.

3. Results and discussion

3.1. *Contact angle measurements*

In our previous paper, it was revealed that the LC alignment regulation depends markedly on the nature of the substituent on the azobenzene moiety [1 (*b*), (*c*)]. A hydrophopic substituent, for example, hexyl on the *trans*-azobenzene moiety, results in a homeotropic alignment, and the subsequent photoconversion into the *cis*-isomer induces the alignment alteration to a parallel mode. Contrary to this, a hydrophilic substituent on the *trans*-azabenzene unit gives no homeotropic alignment so that the photoisomerization into the *cis*-counterpart brings about no distinct LC alignment change. In order to obtain a clue to elucidate the substituent effect on the photoregulation, evaluation of the surface energy of quartz plates modified with azobenzene silylating reagents (**1** and **2**) was undertaken (see figure 2).

It has been already reported that thin films of polymers substituted with azobenzene units demonstrate a similar contact angle change upon photoirradiation [10]. Figure 3 shows the change in static contact angles for water on azo-modified quartz plates upon alternating exposure to UV and visible light for the photoisomerization. The surface of the quartz plates were modified according to our previous paper [1]. A reproducible and distinct alteration of the contact angle was observed upon photoirradiation for a plate modified with a monolayer of the azobenzene substituted with *p*-hexyl chain (**1 a**). The surface possesses larger contact angles for water when the azobenzene units are in the *trans*-form. Other plates displayed a relatively slight change in the contact angles with lower values. This suggest that the hydrophobic *p*-substitutent on the azobenzene moiety is directly exposed to an aqueous phase.

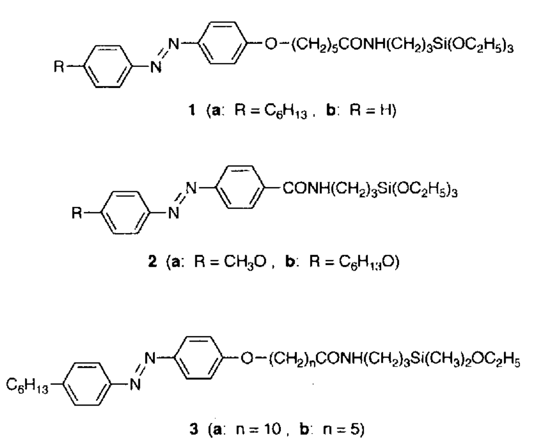

Figure 2. Chemical structures of the azobenzene silylating reagents.

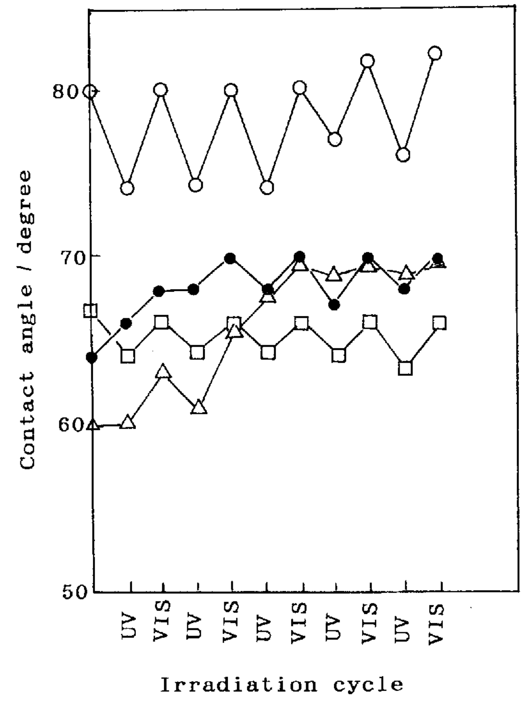

Figure 3. Change in contact angles for water on quartz plates surface-modified with **1 a** (○), **1 b** (●), **2 a** (□) and **2 b** (△).

The results shown in figure 3 seem to be in line with the effect of the substituent on the photoregulation of LC alignment since only the *p*-hexyl substituent is effective for the photoregulation. This appears to confirm the so-called Friedel–Creagh–Kmetz (FCK) rule which claims that LC alignment is governed by the relationship between critical surface energy of substrate (γ_c) and surface tensions of the LC (γ_{LC}); parallel alignment is obtained when γ_c is larger than γ_{LC} while γ_c smaller than γ_{LC} results in homeotropic alignment [11].

In order to determine the validity of the empirical FCK rule, γ_c for the azo-modified plates was estimated according to the Zisman plots [12]. Figure 4 summarizes Zisman plots for a quartz plate (plate 1) modified with *p*-hexylazobenzene silylating reagent (**1 a**) and a plate (plate 2) modified with a 3·4:96·6 mol % mixture of **1 a** and ethyltriethoxysilane (ETS). Irradiation of the plate 1

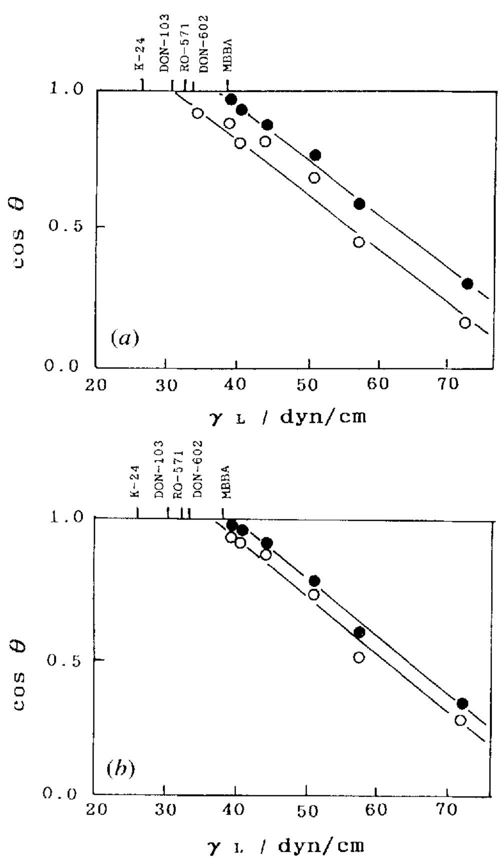

Figure 4. Zisman plots of contact angle θ versus the liquid surface tension γ_L for quartz plates modified with (*a*) **1 a** and (*b*) at 3·6 : 96·6 mixture of **1 a** and ETS before (○) and after UV irradiation (●).

modified solely with **1 a** caused the alteration of the contact angles of reference solvents, and γ_c for the *trans*-azobenzene plate ($\gamma_{c,trans}$) was 30 dye cm^{-1} while the *cis*-plate $\gamma_{c,cis}$ = 37 dye cm^{-1} (see figure 4 (*a*)). If the FCK rule could be applied to the present system, the photoregulation should be induced under condition that $\gamma_{c,trans} < \gamma_{LC} < \gamma_{c,cis}$. Thus, we examined the photoregulation of alignment of various liquid crystals with varying γ_{LC}. These were all active for the alignment alteration upon alternate UV–visible irradiation. These results obviously indicate that the FCK rule does not apply to the azo-modified plate system since the alignment control of both K-24 (γ = 26·2 dyne cm^{-1}) with γ_c smaller than $\gamma_{c,trans}$ and MBBA (γ = 34·2 dyne cm^{-1}) with γ_{LC} larger than $\gamma_{c,cis}$ were photochemically induced by the plates. Furthermore, although the change in γ_c of the plate 2 upon photoirradiation is relatively small, photo-induced alignment change was, in fact, observed for these liquid crystals (see figure 4 (*b*)).

The invalidity of the FCK rule was again confirmed in the case of plates surface-modified with a *p*-hexylazobenzene possessing a dimethylmonoethoxysilyl residue with a decamethylene spacer (**3 a**) (see figure 2). As described in our previous paper [1 (*b*)], the capability of the azobenzene unit for the photoalignment regulation depends not only on the substitutent of the chromophoric moiety, but also on the mode of silylation on the silica surface. No photoregulation was induced by the silylating reagent with a dimethylmonoethoxysilyl group (**3 b**) while **3 a** did work. The difference of the molecular structures of **3 a** and **3 b** is solely in the spacer length between the chromophore and the silylating residue; **3 b** bears a shorter C_5 spacer. In order to obtain further information concerning the effect of the longer spacer, quartz plates were treated with mixtures of **3 a** and ATS in varying ratios. For the evaluation of the capability of **3 a** to bring about a homeotropic alignment, ATS was used here as a two-dimensional dilutant because of its capability to cause a planar mode. Table 1 shows the dependence of photoalignment regulation on the formulation of silyation as well as the contact angle change for water upon alternate UV–visible irradiation. Though no contact angle change was observed for a plate modified with a 5 : 5 or 2 : 8 mixture of **3 a** and ATS, a liquid crystal cell fabricated with the plates displayed distinct alignment alteration between homeotropic/parallel modes upon alternate exposure to UV–visible light (runs 2 and 3).

Table 1. Photo-regulation of liquid crystal alignment by plates modified with **3 a** with or without ATS.

Run no.	**3 a** : ATS	Modifier alignment† VIS	Modifier alignment† UV	Contact angle/degree VIS	Contact angle/degree UV
1	1·0 : 0·0	H	P	71	68
2	0·5 : 0·5	H	P	70	70
3	0·2 : 0·8	H	P	65	65
4	0·1 : 0·9	P	P	49	45

†H and P denote homeotropic and parallel alignment, respectively.

All these data point out that the function of photocontrollable surfaces cannot solely be determined by the photo-induced modification of surface energy.

3.2. *Spectroscopic measurements*

The invalidity of the FCK rule in our photo-active surface systems requires alternative explanation for the working principle of the photo-induced alignment regulation. This situation has led us to measure electronic absorption spectra of the surface-modified plates [13].

Azobenzene have three absorption bands between 200 nm and 500 nm, as presented in figure 5. The visible band at about 440 nm is assignable to the n-π^* transition whereas a band the shorter wavelength correspond to the π–π^* transition [14]. The absorption at about 360 nm is due to the transition parallel to the long axis of the

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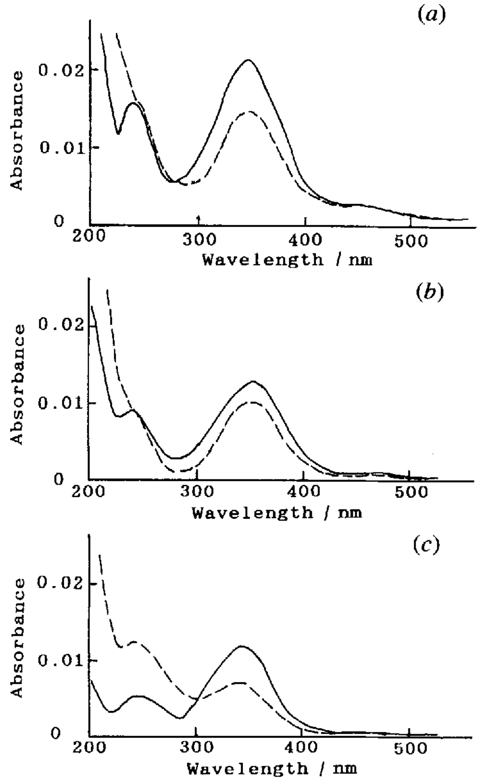

Figure 5. Electronic absorption spectra of azobenzenes of (*a*) plate 1 modified solely with **1 a**, (*b*) plate 3 modified with a 1 : 9 mixture of **1 a** and ETS and (*c*) plate 4 modified with **3 a** before (——) and after (– – –) contact with a liquid crystal (EXP–CIL).

chromophore while the transition owing to the short axis of the chromophore appears at a shorter wavelength of about 250 nm. Thus, the ratio of absorbance (A_s) at the shorter wavelength (λ_s) to that (A_l) at the longer wavelength (λ_l) is an estimate of the orientation of the chromophore. The smaller the value, the larger is the angle between the molecular axis of the chromophore and the substrate surface. In fact, the tilt angle of the azobenzene monolayer in the Langmuir–Blodgett films has been evaluated by measuring the absorbance ratio [15].

In a solution where the molecular orientation is totally random, the ratio (A_l/A_s) of the azobenzene moiety conjugated with an oxygen atom in the *p*-position is 2.22 in ethanol. The slight blue-shift of γ_{max} of plate 1 may be due to the partial formation of the face to face dimer of the chromophore [1 (*a*), (*b*)] while the azobenzene units on plate 3 are mono-molecularly dispersed since the absorption spectrum is quite similar to those in an ethanol solution (see table 2). However, as summarized in table 2, A_l/A_s values for both plates decrease markedly, indicating that predominant portion of the azobenzene units attached to the surface possess a larger tilt angle, which is defined here as an angle between the molecular longer axis of the azobenzene and the substrate surface. This was further confirmed by the dependence of an electronic absorption spectrum on the angle of measuring light, as illustrated in figure 6. The A_l/A_s value for plate 3 increases when the spectrum is measured by light with an incident angle of 45°.

On the contrary, the absorption spectrum of a plate (plate 4) modified with **3** is quite similar to that in ethanol solution with respect to the absorption maxima, as well as the A_l/As value. This reflects the random orientation of the azobenzene units in this case. We found that the contact of the surface with the LC results in an enhancement of the perpendicular reorientation of the azo-chromophore, as follows. Here we used a ternary nematic LC mixture of two cyclohexylhexenes and a cyclohexanecarboxylate (EXP–CIL) which are relatively transparent in the UV region. The absorbance of the LC increases abruptly below about 250 nm. Since the LC displays a positive absorbance at λ_s, the estimation of A_l/A_s for plates wetted with the liquid crystal lacks accuracy. It follows that instead of A_s, the absorbance (A_{250}) at 250 nm is adapted to estimate the orientation of the azobenzene on the surface by calculating A_l/A_{250} since the contribution of the absorption by the liquid crystal on the surface at 250 nm is negligibly small. This was confirmed by measuring the absorbance at

Table 2. Electronic absorption properties of azobenzene.

	Absorption maxima/nm			A_l/A_{250}	
	λ_s	γ_l	A_l/A_s	Without LC	With LC
In ethanol	237	347	2·27	—	—
Plate 1	240	343	1·33	1·45	1·11
Plate 3	238	349	1·42	1·83	1·62
Plate 4	238	348	2·17	2·37	0·61

λ_s: Shorter absorption wavelength; λ_l: longer absorption wavelength; A_l: absorbance at the longer wavelength; A_s: absorbance at shorter wavelength; A_{250}: absorbance at 250 nm.

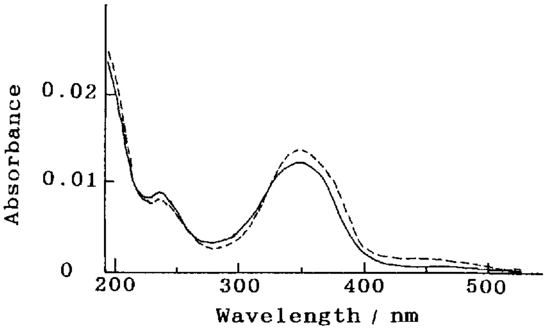

Figure 6. Electronic absorption spectra of the azobenzene of plate 3 modified with a 1 : 9 mixture of **1 a** and ETS with incident angle of measuring light at 0° (——) and 45° (– – –) to normal, respectively.

250 nm of an LC layer of 0·1 mm thickness = 0·066; the absorption coefficient is about 0·2 at this wavelength. The A_l/A_{250} values are given in Table 2. The results imply that the contact of the surface with the LC brings about the enhancement of perpendicular reorientation of the chromophore. This is in accordance with observations in LB films incorporating azobenzene units [7]. Particularly it should be noticed that the A_l/A_{250} value of plate 4 changes upon contact with the LC. This supports the fact that the orientation of the azo-chromophore perpendicular to the surface is dramatically induced by the interaction with LC molecules. Consequently, the transformation of the *trans*-form of azobenzene groups brings about the rearrangement of the LC molecules surrounding the azo-choromophore leading to the alignment alteration of the bulk LC molecules. Although surface energy corresponds to one of the important macroscopic properties, it does not control orientation at a molecular level.

3.3. *Rubbed surfaces*

The UV exposure of the azo-modified plates results in the formation of planar LC alignment, but the direction of the LC molecules is not uniaxial so that the mesophase displays a multi-domain structure. On the other hand, as described in our previous paper [3 (*a*)], the homogeneous alignment after UV exposure has been achieved by rubbing a poly(vinyl alcohol) thin film which is surface-modified with azobenzene units or by transferring Langmuir–Blodgett membranes on to a substrate plate [4].

A recent paper has revealed that irradiation with linearly polarized UV light offers a unique technique to induced homogeneous alignment [16].

It is well-known that the rubbing treatment of glass surfaces affords a homogeneous alignment of LCs [11]. Based on these facts, an alternative way to achieve photo-induced homogeneous alignment was attempted here by rubbing a quartz substrate with polishing powders before the surface modification with the azobenzene (**1 a**). A LC cell was fabricated with a pair of rubbed, azo-modified plates so that the rubbing directions were parallel. Before UV irradiation, the action of the azobenzene tethered from the surface wins over the rubbing treatment so that the alignment was homeotropic. A planar alignment was brought about upon exposure to UV light. A monitoring He–Ne laser beam was passed perpendicularly through the irradiated cell placed between two crossed polarizers and rotated around the beam axis to follow the relationship between transmitted light intensity and rotation angle. The result is shown in fig. 7. Although the contrast is relatively poor, the appearance of the intensity maximum at around 45° indicates that the alignment direction of the LCs is parallel to the rubbing direction. The effect of the rubbing treatment was further confirmed by constructing a 90° twisted nematic LC cell in which the rubbing direction of the plates was set perpendicularly to each other. The cell demonstrated an optical rotation power of 87° after UV irradiation while very weak optical rotation of 0·044° was observed before irradiation because of the homeotropic alignment.

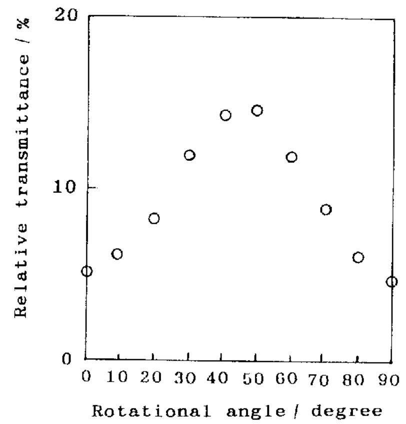

Figure 7. Transmitted intensity of a probing He–Ne laser beam through a UV irradiated cell between polarizers as a function of the rotational angle of the cell.

Table 3. Polarized electronic absorption bands of a rubbed quartz plate surface-modified with an azobenzene silylating reagent (**1 a**).

Direction of polarization plane	Absorbance† Before UV irradiation A_s			Absorbance† After UV irradiation A_s	
	A_s	A_l	A_l/A_s	A_s	A_l
Parallel to rubbing direction	0·026	0·017	0·64	0·027	0·014
Perpendicular to rubbing treatment	0·028	0·019	0·67	0·028	0·013

† A_s: absorbance at the shorter wavelength; A_l: absorbance at the longer wavelength.

In order to reveal the factors determining the homogeneous alignment, electronic absorption spectra of the plates, which were rubbed before the azo-modification, were measured. Table 3 summarizes the results, which show that there is no marked dichroism both before and after UV irradiation. This fact verifies that the rubbing treatment results in no anisotropic orientation of the azobenzene chromophores. Recent investigations of the orientation of LC molecules at the substrate surface by means of surface second harmonic generation spectroscopy have revealed two kinds of alignment mechanisms [17]. The first one is based on the long range order of LC molecules which orient along grooves formed by the rubbing treatment without any specific interaction be-

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tween silica surface and LC molecules. On the other hand, the homogeneous alignment induced by rubbed polyimide arises from short range order due to strong molecular interactions between the polymer chains and LC molecules at the interfacial region. Thus, photo-induced homogeneous alignment is caused not by the arrangement of the chromophore, but possibly by the action of grooves on the surface according to the former aligning mechanism.

4. Conclusions

The wettability of quartz plates surface-modified with azobenzene was altered reversibly by alternate exposure to UV and visible light to bring about the photoisomerization. The extent of the wettability alteration was specifically dependent on the substituent on the azobenzene chromophore and the mode of the covalent bonding upon the surface. Critical surface energies for the plate modified with *p*-hexylazobenzene, which displayed the largest contact angle change, were estimated before and after UV irradiation. There was no distinct mutual relationship between the surface energy and surface tension energy of LCs. Furthermore, the surface modified with another type of azobenzene silylating reagent was able to trigger the photochemical alteration of LC alignment although no essential contact angle change was observed upon photo-irradiation. These facts reveal that the so-called FCK rule to determine LC alignment does not govern photo-active surface function. On the other hand, it was found that electronic absorption spectra of the azo-modified plates are affected by contact with an LC layer and suggests that the surface azobenzene units reorient upon the contact with LC molecules. This supports the existence of strong interactions between the azobenzene groups and LC molecules at the boundary region. The surface photo-orientation arises thus from specific molecular interactions which are altered by the photoisomerization of azo groups.

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