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A convenient preparation of photoactive monolayers for liquid crystal photoalignment by the surface adsorption of an aminoalkylated azobenzene on poly(acrylic acid) films

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Spin-cast poly(acrylic acid) (pAA) films on a substrate plate are immersed in a hexane solution of 4-butyl-4′-(10-aminodecyloxy)azobenzene, resulting in surface-selective adsorption and leading to the formation of photoactive monolayers. The surface adsorption behaviour is critically affected by the concentration of the azobenzene adsorbate solutions, and a 2.5×10^{-5} mol dm^{-3} solution gives an azobenzene monolayer with a surface density of 2 molecules nm^{-2} without any modification of the surface morphology of the pAA film. The surface density of the azobenzene is controlled by a binary system consisting of the azobenzene and *n*-octadecylamine. Photoirradiation of the surface-modified film with linearly polarised UV light for *E*-to-*Z* photoisomerisation results in the orientational transformation of the nematic liquid crystal layer from homeotropic to homogeneous alignment. It has been found that the minimum exposure energy of polarised UV light required for the liquid crystal alignment photocontrol is determined by the surface density of the azobenzene. There is a critical density; no photoresponse is observed for average densities of the azobenzene smaller than *ca.* 0.7 molecules nm^{-2}. With densities larger than this value, the smaller the density of the chromophore on pAA surface is, the faster the photoreorientation of the liquid crystal effectively takes place.

Photocontrol of the orientation of nematic liquid crystals (LCs) by photoinduced structural alteration of molecular and polymeric layers (command layers) on substrate surfaces[1] has been extensively studied because of its applicability to the fabrication of optical elements and devices based on the photo-optical effect[2] and to the production of LC aligning layers normally made *via* the conventional rubbing procedure.[3] Since the surface-settled photocontrol of LC alignment is determined specifically by photoisomerisable moieties at the uppermost surfaces, the preparation of monomolecular command layers plays a key role in device-oriented development of photoresponsive LC cells. They have so far been provided by chemisorption of photochromic silylating reagents on a silica surface,[4] surface-selective chemical modification of polymer surfaces,[5,6] monolayered deposition of photochromic polymers by means of the Langmuir–Blodgett technique[7,8] and spin-coating of photochromic polymers.[9,10]

The marked molecular amplification of structural modification of command layers has been reasonably interpreted in terms of the minimisation of the elastic energy of LCs. Taking notice of this fact, the macroscopic LC alignment gives us a novel clue to obtain information concerning microscopic as well as mesoscopic behaviour of self-assembled monolayer (SAM) systems,[11] which have been attracting increasing interest in respect of their applicability to chemical sensors,[12] nonlinear optical materials,[13] photolithographic materials[14] and so on. Representative procedures to prepare SAMs involve the covalent adsorption of organic molecules on crystal lattices of metals and metal oxides, including, for example, the reaction of alkanethiols with Au or Ag,[15,16] and phosphonates on metal phosphonates,[17] and the adsorption of carboxylic acids on metal oxides.[18] On the other hand, except for silane coupling on silica surfaces,[11,19] there have been no versatile and practical procedures to give SAMs on amorphous inorganic surfaces by monolayered adsorption. Besides, to the best of our knowledge, no systematic studies on the fabrication of SAMs on the surface of polymer films *via* immersion of an amorphous polymer film into a solution of suitable molecules have been carried out, although the process would seem to be of significance due to its wide range of applicability.

We have achieved previously the surface-selective acetalisation[5] and esterification[5,6] of poly(vinyl alcohol) (PVA) thin films for the covalent attachment of azobenzene residues to prepare command layers for the photocontrol of LC alignment. It was revealed that the surface of amorphous PVA films deteriorated to a greater or lesser extent as a result of chemical surface transformation.[6] These results led us to explore an alternative route to surface-selective adsorption under milder conditions to form photoresponsive SAMs incorporating azobenzene moieties. In a series of studies on surface modification *via* hydrogen bond formation, we recently reported that aminoalkylated azobenzenes adsorb on a polar silica surface *via* hydrogen bonds and proposed a convenient way to fabricate photoresponsive LC cells.[20] This procedure has a drawback, however, due to the relatively weak hydrogen bonds, so that the photocontrollability of substrate plates adsorbing aminoazobenzenes disappears upon prolonged storage because of desorption.

The purpose of this report is to provide a convenient method for the preparation of photoresponsive SAMs acting as command layers *via* hydrogen bond formation between aminoalkylated azobenzene molecules and carboxy groups at the outermost surface layer of poly(acrylic acid) (pAA) films, thus giving durable photoresponsive LC cells. The surface-selective adsorption of an aminoalkylated azobenzene was markedly influenced by the nature of the solvents used and the concentration of the azobenzene adsorbate. Surface-selective adsorption under appropriate conditions yielded efficient command layers which were sensitive to linearly polarised UV light, thus giving azimuthal control of LC alignment.

Experimental

Materials

The chemical structures of the materials used in this study are presented in Fig. 1. pAA (Aldrich: 25 wt% aq. solution, *M*w =

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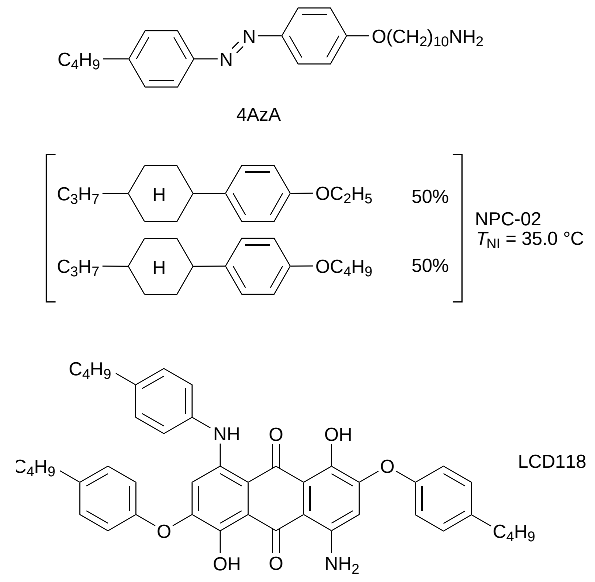

Fig. 1 Chemical structures of materials

ca. 2.4 × 10^5) was used as received. *n*-Octadecylamine (C18A) was obtained from Kanto Chemical Co. Inc., and purified by distillation. 4-(10-Aminodecyloxy)-4′-butylazobenzene (4AzA) was prepared according to a previous procedure.[20] A nematic LC (NPC-02), a binary mixture of alkoxyphenylcyclohexanes (T_{NI} = 35.0 °C), was donated by Rodic Co. Ltd., and used as received. Spherical glass spacers of a 5 µm diameter were suspended in the LC for the adjustment of the cell gap. A dichroic diaminoanthraquinone dye (LCD118) as a guest was a gift from Nippon Kayaku Co., Ltd. The LC was doped with 1 wt% of the dichroic dye for the determination of the LC alignment director.

Surface modification

Quartz plates were cleaned in the same manner as described previously and used immediately.[20] A 1 wt% aq. solution of pAA was filtered through a hydrophilic PTFE type membrane filter with a 0.2 µm pore size and spin-cast on 1 × 3 cm^2 quartz plates, followed by drying *in vacuo* for 1 h at 100 °C. Film thickness in the range 25–30 nm was measured by DEKTAK 3ST (Japan Vacuum Technology Co.). Plates coated with pAA films were immersed in a hexane solution (2.5×10^{-4} or 2.5×10^{-5} mol dm^{-3}) of 4AzA at 40 °C, rinsed with fresh hexane three times, and dried for 1 h at 100 °C. The co-adsorption of 4AzA with C18A was performed under the same conditions for the adsorption of 4AzA.

Physical measurements and photoirradiation

Absorption spectra of films adsorbing 4AzA were taken on a MAC-1 type weak absorption spectrometer (JASCO). Atomic force microscopy measurements were performed using an AFM SPA300 instrument from Seiko Electronics Co. Photoirradiation was carried out with a Hg–Xe lamp (Supercure-203S, San-ei Electric MFG. Co.). Linearly polarised light was obtained by passing light through a Glan–Thomson prism.

Liquid crystal photoalignment

A hybrid type guest–host (GH) LC cell was fabricated with an azo-modified pAA plate and a quartz plate modified with lecithin and exposed to linearly polarised light according to our conventional procedures.[6,8,9] Linearly polarised 365 or 436 nm light was obtained by passing light from a 500 W ultra-high pressure mercury arc (USHIO Inc.) through a combination of glass filters (Toshiba, UV-D36A + UV-35 or V-44 + Y-43) and a polariser. An irradiation angle (θ) is defined here as the angle between the electric vector of actinic linearly polarised light and the tentative LC cell axis which is in parallel with the longer axis of a rectangular LC cell, as shown in Fig. 2(*a*). Photoinduced LC alignment induced by the LPL irradiation was monitored by measuring the light intensity of the probing polarised He–Ne laser beam passed through the cell and a crossed analyser as a function of the rotational angle (Φ) of the cell around an experimental optical axis as sketched in Fig. 2(*b*).

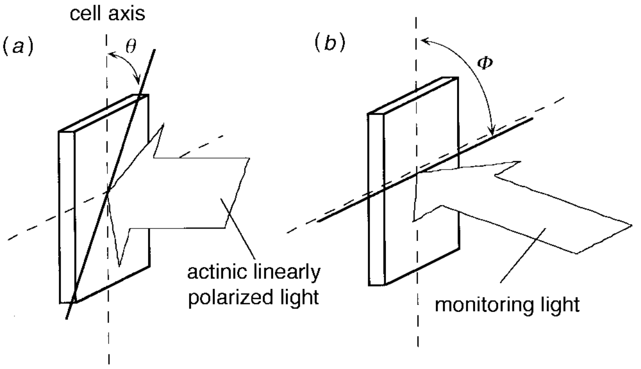

Fig. 2 Irradiation conditions for (*a*) the generation and (*b*) the determination of LC photoalignment

Results and Discussion

Surface adsorption

The adsorption of organic molecules *via* hydrogen bonds as well as coulombic interactions is the principle of dyeing of polymeric materials, so that the surface-selective adsorption on polymer surfaces is usually of less significance in order to obtain sufficient colorisation. Despite extensive studies of the physical as well as chemical adsorption of low-mass molecules on inorganic and metallic surfaces,[11] only a few reports have been made on surface-selective adsorption onto polymer films to perform material functionalisation.[21]

A pAA thin film of about 25 nm in thickness on a quartz plate was immersed in a 2.5×10^{-4} mol dm^{-3} toluene solution of 4AzA, and the amount of azobenzene on the polymer surface was followed at intervals by UV spectral measurement. Absorbance of 4AzA adsorbed on the pAA film surface increased during the early stages of the immersion period, followed by an abrupt decrease through a maximum value. This implies that the binding of azobenzene moieties to polymer chains *via* hydrogen bonds results in the enhanced solubility of a resultant polymer complex, which dissolves in the solvent. No reproducible result for the surface adsorption of azobenzene in toluene was obtained even though conditions, including dipping period, concentration and temperature, were controlled carefully. It followed that hexane was employed as the poorer solvent. Fig. 3 shows the adsorption behaviour of 4AzA on a pAA film from hexane solution at 40 °C. Under the assumption that the absorption coefficient of the azobenzene is not much altered by the surface adsorption, average densities of the adsorbate were estimated spectroscopically and plotted against immersion periods. The adsorption of 4AzA levelled off after *ca.* 15 min to give a constant value in dilute solutions, although it was dependent on the concentration. The average densities were about 2 and slightly larger than 5 molecules per nm^2 in 2.5×10^{-5} and 2.5×10^{-4} mol dm^{-3} solutions, respectively. Although these values are only approximate, since the absorption spectra of adsorbed 4AzA were slightly modified owing to intermolecular interactions of the chromophore (as mentioned later), they may be valid for the following semi-quantitative discussion.

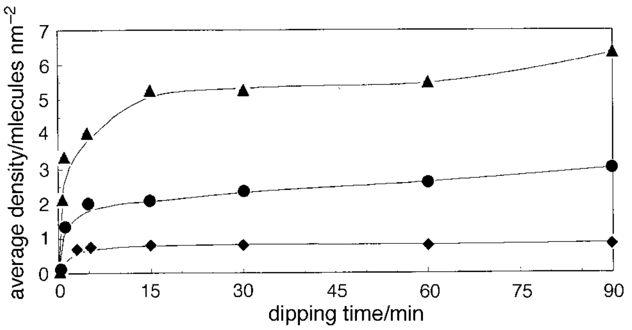

Fig. 3 Average densities of 4AzA on pAA films immersed in (▲) 2.5×10^{-4} and (●) 2.5×10^{-5} mol dm^{-3} hexane solutions of 4AzA and (◆) a 2.5×10^{-5} mol dm^{-3} hexane solution of an equimolar mixture of 4AzA and C18A

Atomic force microscopy (AFM) measurements showed that the surface morphology is also dependent on the concentration of the azobenzene solution in hexane, as presented in Fig. 4. Although the surface of the spin-cast pAA film was slightly uneven to begin with, the surface roughness increased markedly when the film was dipped in a 2.5×10^{-4} mol dm^{-3} solution of 4AzA. Many protuberant peaks a few nanometres in height were generated, as shown in Fig. 4(*b*), where the lateral size has been reduced in proportion to the height. It is very likely that the surface roughness observed here arises from an excess amount of adsorbed azobenzene, leading to the enhancement of the solubility of the polymer chains and swelling in hexane. In contrast, the surface morphology of this film was essentially unmodified after the immersion in a 2.5×10^{-5} mol dm^{-3} solution.

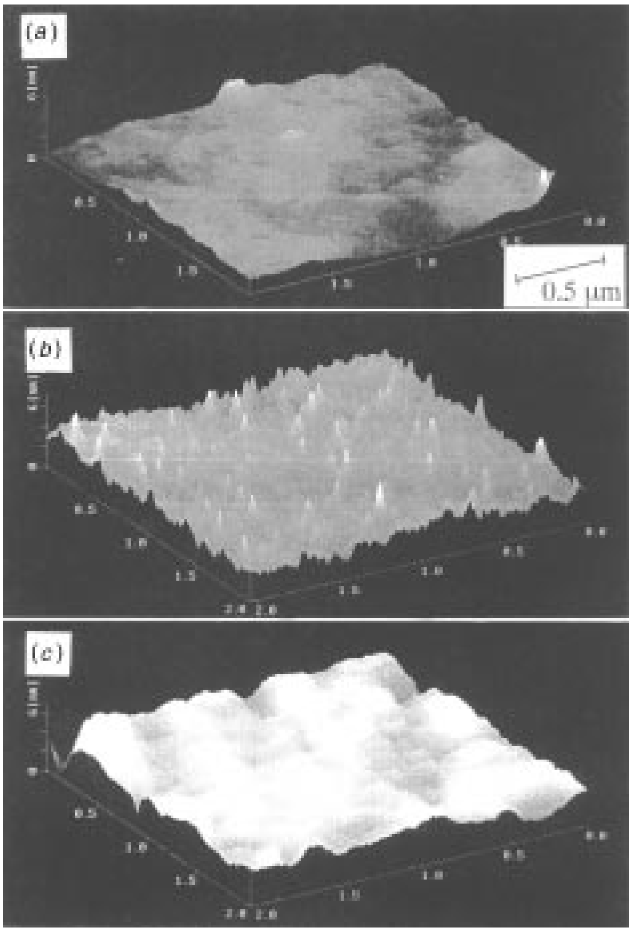

Fig. 4 AFM images of (*a*) a spin-cast pAA film, and pAA films formed by dipping in (*b*) 2.5×10^{-4} and (*c*) 2.5×10^{-5} mol dm^{-3} hexane solutions for 15 min, respectively. The lateral size is 2×2 μm^2 and maximum height is 6 nm.

These results imply that the adsorption of 4AzA takes place specifically on the surface to form a SAM from a solution of the lower concentration, *i.e.* 2.5×10^{-5} mol dm^{-3}. It was reported that the population of polar OH groups at the uppermost surface of a poly(vinyl alcohol) film is estimated to be 2.7 and slightly larger than 2 units nm^{-2} on the basis of surface-selective modification of the film with isocyanates[22] and azobenzene acid chlorides,[6] respectively. These values are not far from the present one, implying that the adsorption of the azobenzene takes place specifically on the film surface of the vinyl polymer bearing polar carboxy residues.

The surface density of the azobenzene is controlled using a binary system. As given in Fig. 3, the averaged density of surface azobenzene was reduced and estimated to be about one third of that for a 2.5×10^{-5} mol dm^{-3} hexane solution of 4AzA when the pAA film was immersed in a 2.5×10^{-5} mol dm^{-3} hexane solution of an equimolar mixture of 4AzA and octadecylamine (C18A). The adsorption of 4AzA was saturated within 5 min, and no increase in the adsorbate was observed upon even prolonged immersion, indicating that a SAM consisting of a binary component had been prepared.

Surface photochemistry

Fig. 5 shows the absorption spectra of azobenzene adsorbed on a pAA film and in hexane as a control before and after photoirradiation. The results are summarised as follows. First, the azobenzene adsorbed from a 2.5×10^{-5} mol dm^{-3} solution forms an aggregate, as elucidated by a significant blue shift of the π-π^* absorption band at 332 nm [Fig. 5(*a*)] when compared with a spectrum in a hexane solution [Fig. 5(*c*)]. The blue-shifted absorption maximum is assignable to a face-to-face aggregate of Az units.[23] The chromophores were decoupled by successive UV and visible irradiation to give an photostationary state containing the *E*-isomer as the major component. These spectroscopic behaviour is similar to azobenzene adsorbed on a silica surface, as described in our previous paper.[4] The aggregation was efficiently suppressed by the co-adsorption of 4AzA and C18A, as seen in Fig. 5(*b*), where $\lambda_{\max}$ was not much different from those in solution and of the film at an *E*-isomer-rich photostationary state. Second, as revealed by comparison with solution photochemistry, the transformation of the *E*-isomer is suppressed to give a reduced level of the *Z*-isomer portion (*ca.* 30%) at the photostationary state [Fig. 5(*a*)]. This situation is not much different from the photochemistry of 4AzA in a film prepared from a binary system [Fig. 5(*b*)]. All these results suggest that photoisomerisation upon irradiation with 365 nm light is influenced by the two-dimensional free volume in the adsorbed monolayers.

Photoreaction of 4AzA-film

It is well-known that polarised irradiation of polymeric films incorporating azobenzenes induces optical anisotropy to generate dichroism as well as birefringence.[24] Similar polarisation photochromism has been observed in azobenzene monolayers tethered to silica surfaces.[4a] In connection with the photocontrol of azimuthal orientation of a nematic LC with linearly polarised light (LPL) irradiation, the polarisation photoisomerisation of azobenzene on a surface was monitored by following dichroic ratios (DR) as a function of the exposure energy of the LPL. DR is defined in eqn. (1):

$$\mathrm{DR}=(A_{\perp}-A_{\parallel})/(A_{\perp}+A_{\parallel}) \qquad (1)$$

where $A_{\perp}$ and $A_{\parallel}$ are the absorbances at 332 nm using polarised probe light with electric vectors perpendicular and parallel to that of actinic LPL, respectively. Fig. 6 shows the generation of DR of a 4AzA-monolayered film prepared from a 2.5×10^{-5} mol dm^{-3} solution upon irradiation with LPL at 436 nm as a

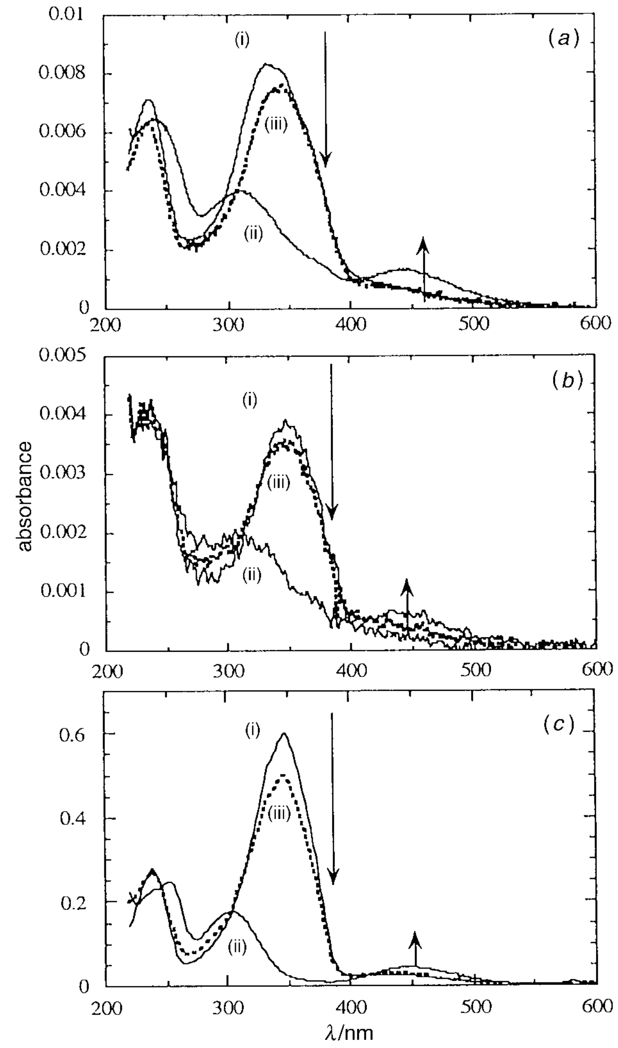

Fig. 5 Absorption spectra of 4AzA adsorbed on pAA films (*a*) from a 2.5×10^{-5} mol dm^{-3} hexane solution of 4AzA, (*b*) from a 2.5×10^{-5} mol dm^{-3} hexane solution of an equimolar mixture of 4AzA and C18A and (*c*) a hexane solution of 4AzA, (i) before and (ii) after irradiation with 365 nm light and (iii) after subsequent irradiation with 436 nm light

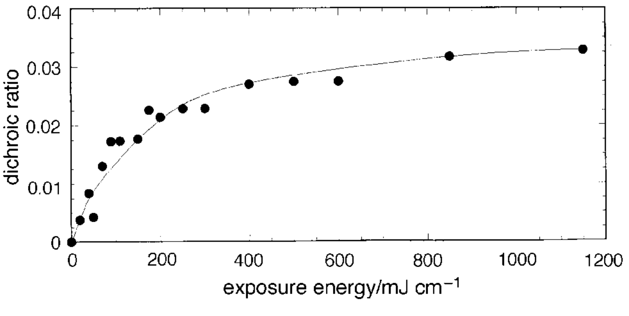

Fig. 6 The generation of dichroism of 4AzA adsorbed on pAA films as a function of exposure energy upon irradiation with polarised 436 nm light

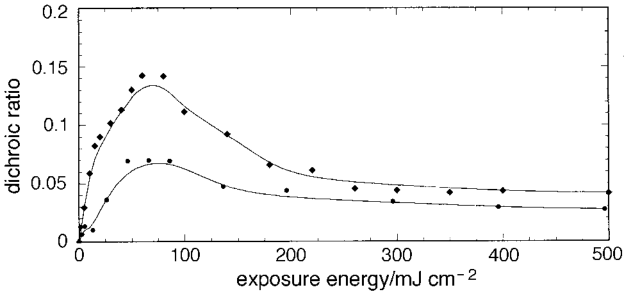

Fig. 7 The generation of dichroism of 4AzA adsorbed on pAA films (●) from a 2.5×10^{-5} mol dm^{-3} solution of 4AzA and (◆) a 2.5×10^{-5} mol dm^{-3} solution of an equimolar mixture of 4AzA and C18A, as a function of exposure energy upon irradiation with polarised 365 nm light

function of exposure energy. Note that n-π^* excitation at this wavelength leads to the predominant formation of the *E*-isomer at the photostationary state. Although DR values are small, the optical anisotropy increases in a linear manner, suggesting that azobenzene moieties in the SAM reorient perpendicularly to the electric vector of actinic visible light. When a 4AzA-monolayered film was illuminated with polarised 365 nm light, a maximum of DR was observed at an exposure energy of *ca.* 100 mJ cm^{-2}, followed by a gradual decline, as shown in Fig. 7. Although this behaviour was not altered by the co-modification with C18A, the dichroic ratio of co-adsorption was twice as large as that of mono-adsorption. The appearance of a maximum DR value can be explained in terms of the involvement of two processes, consisting of axially destructive photoisomerisation and LPL-induced molecular reorientation.[9c] The axially selective *E*-to-*Z* photoisomerisation occurs at the early stage of irradiation with LPL at 365 nm, since the molar absorption coefficient at 365 nm of the *E*-isomer is about 16 times larger than that of the Z-isomer. Consequently, the gradual reorientation of azobenzene units takes place to reach a constant DR value.

Alignment photocontrol

It has been reported that the *E*-to-*Z* photoisomerisation of surface azobenzenes chemisorbed *via* silylation leads to transformation of the homeotropic alignment of nematic LCs into a planar alignment, whereas the planar orientation becomes uniaxial to give homogeneous alignment when actinic UV light is linearly polarised.[25] The same situation resulted from 4AzA monolayers. An LC cell was assembled using a substrate plate coated with a 4AzA monolayer and irradiated with linearly polarised 365 nm light. The LC cell was in homeotropic alignment before photoirradiation, and optical anisotropy emerged upon LPL irradiation, as shown in Fig. 8. The birefringence due to homogeneous alignment was monitored by measuring the transmittance of linearly polarised He–Ne laser light through the cell and a crossed polariser as a function of the rotational angle of the cell. The optical contrast, defined as a ratio of the maximum to the minimum in transmittance, increased with an increase in exposure energy and levelled off at an exposure energy of about 200 mJ cm^{-2}. The orientational direction of the LC was changed by rotating the electric vector

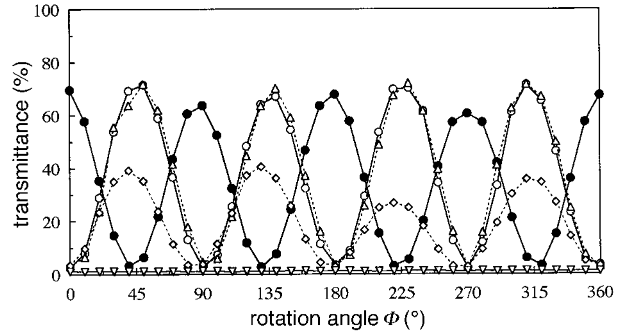

Fig. 8 Angular dependence of transmittance of a monitoring He–Ne laser beam (633 nm) through an LC cell surface-modified with a 4AzA-pAA film (▽) before and after successive irradiation with polarised 365 nm light of exposure energies of (◇) 100, (△) 200 and (○) 300 mJ cm^{-2} at $\theta=0°$, and (●) after subsequent irradiation at $\theta=45°$

of the actinic UV light by 45°, as shown in Fig. 8, indicating that the direction of LC alignment is regulated by the polarisation plane of the UV light. The LC alignment direction can be determined definitely by measuring the photoinduced dichroism of the guest dye. The result given in Fig. 9 indicates that the direction of LC alignment is perpendicular to the electric vector of the actinic LPL, in a manner similar to other systems.[6,8,9] The homogeneous alignment was reversed to a homeotropic one by irradiation with non-polarised 436 nm light of exposure energy of about 60 mJ cm^{-2}. The LC alignment between homeotropic and homogeneous modes was reversible upon alternate irradiation with UV and visible light.

It was found that the exposure energy required for the generation of homogeneous alignment is considerably reduced when the LC cell is fabricated using a plate modified with a 1:1 mixture of 4AzA and C18A. The in-plane anisotropy induced by polarised 365 nm light irradiation was saturated at a lower exposure energy (50 mJ cm^{-2}) when compared with the result for a 4AzA-monolayered film. This observation led us to examine the effect of the surface density of the azobenzene on the minimum exposure energy required for the photocontrol of in-plane LC alignment. The surface density was adjusted by the ratio of 4AzA to C18A. Fig. 10 shows the results. An increase in the density of the azo-chromophore caused a slower photoresponse, while the exposure energies required to induce LC alignment were low, at 1 unit nm^{-2} or less. However, no LC alignment alteration was generated when the density of the azobenzene was less than 0.7 molecules nm^{-2}. These results are in line with those obtained for silica plates surface-modified with azobenzenes *via* silylation.[4a]

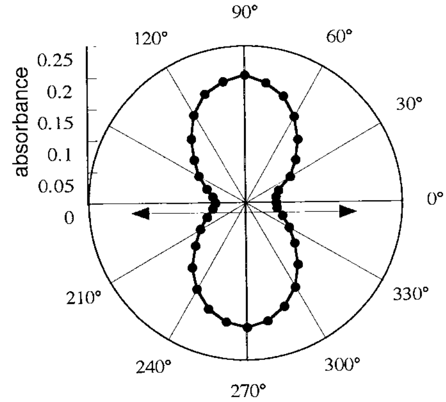

Fig. 9 The circular diagram of absorbances at 633 nm of a dye-doped guest–host LC cell surface-modified with a 4AzA-pAA film after irradiation with polarised 365 nm light (exposure dose 100 mJ cm^{-2})

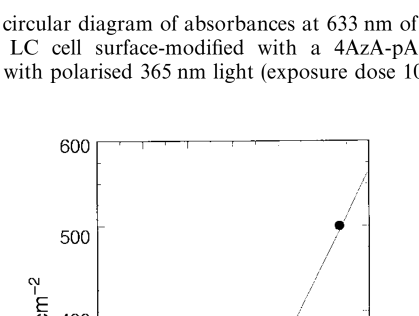

Fig. 10 Exposure doses of polarised 365 nm light required for homogeneous alignment as a function of two-dimensional concentration of 4AzA on pAA films

It should be stressed here that LC cells exhibit excellent performance, including high resolution. Lines and spaces of 2 µm were resolved when an azobenzene monolayer was illuminated with polarised UV light through a photomask, followed by cell assembly. Furthermore, cells worked well even after storage for several months. This is in a marked contrast to our previous report; when the bare surface of a silica substrate plate is treated with an aminoalkylated azobenzene, the LC cell becomes photoinactive after a few days due to desorption. These results suggest that the adsorption of azobenzene on a pAA film surface *via* hydrogen bonds is a convenient and promising way to fabricate command layers.

Conclusion

We have developed a convenient method for preparation of command layers for the photocontrol of liquid crystal alignment by surface adsorption of films of pAA with an aminoazobenzene. The surface morphology of the polymer films is critically affected by the concentration of the azobenzene adsorbate in hexane. Surface-selective adsorption gives SAM systems embedding the photoisomerisable unit under appropriate conditions. Whereas the level of *E*-to-*Z* photoisomerisation in a SAM film on a pAA film is partially suppressed due to the two-dimensional free volume, polarised light irradiation generates dichroism of the chromophore. Irradiation of an LC cell assembled with a plate modified with the azobenzene film generates homogeneous alignment with excellent optical quality and high resolution power.

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