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Surface-Selective Modification of Poly(vinyl alcohol) Films with Azobenzenes for In-Plane Alignment Photocontrol of Nematic Liquid Crystals[†]

Haruhisa Akiyama, Masayuki Momose, and Kunihiro Ichimura*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Shigeo Yamamura

Chemical Research Laboratory, Nippon Kayaku Company, Ltd.,
Shimo-cho, Kita-ku, Tokyo 115, Japan

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ABSTRACT: A surface of poly(vinyl alcohol) (PVA) was treated with an azobenzene acid chloride in hexane in the presence of pyridine to achieve surface-selective introduction of the photoisomerizable azo units. The surface reaction is affected by the solvent, saponification degree of PVA, structure of the acid chloride, and reaction period. Surface morphology of the modified PVA thin films was examined by means of atomic force microscopy. Under optimized reaction conditions, a PVA surface was covered with an average of about 3 azobenzene units per 1 nm^2 to afford a film with excellent flatness. The azo-modified PVA films were employed to regulate in-plane alignment of a nematic liquid crystal by irradiation with linearly polarized light of a hybrid cell which was fabricated by putting a liquid crystal between a glass plate covered with the modified PVA film and a glass plate which was treated with lecithin for a homeotropic alignment. The efficiency of the photoregularity for azimuthal reorientation of liquid crystal was markedly dependent on the molecular structure of azobenzenes. Various properties of the photoresponsive liquid cells are presented.

Introduction

Surface-assisted alignment regulations of nematic liquid crystals (LCs) have been obtained by irradiation with light for the photoisomerizations of photochromic molecules such as azobenzenes which are covalently attached onto substrate surfaces.[1] There are two types of photochemical alignment alteration depending on whether actinic light is linearly polarized. The first involves the reversible modification of LC orientation between homeotropic and planar modes upon exposure to nonpolarized light,[2] whereas linearly polarized light leading to photochromic reactions of surface molecules results in in-plane reorientation of LC molecules[3–6] which is controlled by changing the electric vector of actinic light. The latter type of alignment regulation possesses practical significances for applications to optical memory and photon-mode display devices since optical information is written-in and overwritten with linearly polarized light from a single light source.

Our recent work has shown that the photochemical in-plane reorientation of nematic LCs is achieved by assembling LC cells with use of silica plates which are surface-modified with photochromic units including azobenzenes[5,6] and a spiropyran.[7] Since the alignment mode should be planar for the azimuthal photoregulation, lateral attachment of azobenzene chromophores on silica substrate surfaces affords an effective strategy for the alignment regulation because the long molecular axis of the photochromic moiety may lie parallel with the substrate surface to result in a planar alignment.[5] On the basis of these results, we have proposed a concept of a molecular rotor[5] which is bound on a substrate surface and rotates around a molecular axis linking the rotor on the surface by linearly polarized light. This paper deals with the photoregulation of in-plane LC reorientation triggered by azobenzenes laterally attached to a poly(vinyl alcohol) (PVA) thin film instead of a silica plate.[8] Because the LC alignment regulation is brought about by azobenzene units localized on an uppermost surface layer of a substrate plate, surface-selective modification of PVA films with azobenzenes will be treated in more detail, followed by the reorientation behavior of LC contained in a cell fabricated with the azo-modified PVA films.

Experimental Section

Fully saponified PVA with a polymerization degree = 2000 (NH-20) and partially (80%) saponified PVA with polymerization degree = 1700 (KH-17) were commercially available from Nippon Synthetic Chem. Ind. Co., Ltd., and were purified by precipitating aqueous solutions into methanol. All LCs were donated by Rodic Co., Ltd., and used as received. The structures are shown in Figure 1.

4-Hexyl-2′-[(10-carboxydecyl)oxy]-4′-(hexyloxy)azobenzene (1: C6AzOC6sC10). The compound was prepared as previously described,[5] starting from resorcinol monobenzoate. λ_{max} (ϵ) in ethanol: 364 nm (1.82 × 10^4).

2-[(10-Carboxydecyl)oxy)-5-methylazobenzene (2: AzOC1sC10). A mixture of 2.0 g of 2-hydroxy-5-methylazobenzene, 3.0 g of tetrahydropyranol 11-bromoundecanoate, and 2.0 g of potassium carbonate in 8.0 mL of DMF was stirred at 60 °C for 10 h, followed by dilution with ether and washing with dilute hydrochloric acid and water. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed to give a crystalline mass which was purified by column chromatography on silica gel with use of a 1:20 (v/v) mixture of hexane and ethyl acetate and by recrystallization from methanol to give 1.1 g of orange crystals of mp 57–58 °C. Found: C, 72.59; H, 7.94; N, 7.05. Calcd for $C_{24}H_{32}O_3O_2$: C, 72.69; H, 8.14; N, 7.07. ^{1}H-NMR ($CDCl_3$): δ 1.10–1.70 (m, 16H, $-CH_2-$), 2.32 (t, 2H, $-CH_2COO-$), 2.32 (s, 3H, aromatic CH_3), 4.13 (t, 2H, $ArOCH_2-$), 6.95 (d, 1H, aromatic H), 7.18 (d, 1H, aromatic H), 7.35–8.0 (m, 6H, aromatic H). λ_{max} (ϵ) in ethanol: 314 nm (1.28 × 10^4).

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* To whom correspondence should be addressed.

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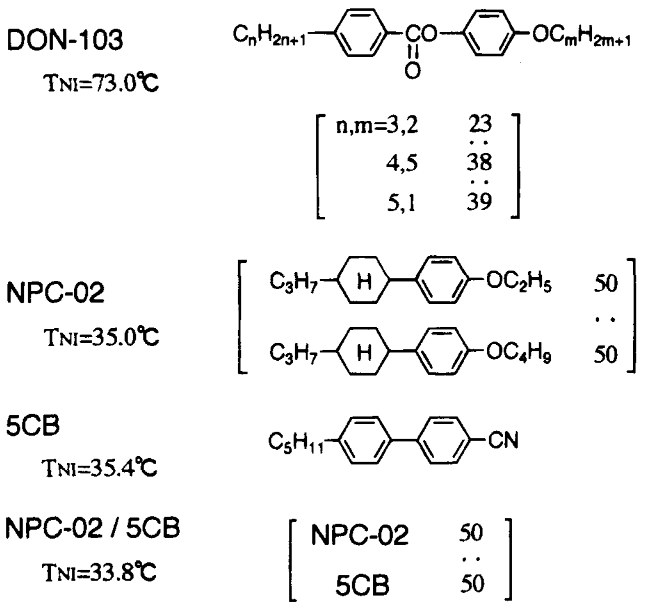


Figure 1. Structures of LCs.

2-(Carboxymethoxy)-5-methylazobenzene (3: AzO-C1sC1). A mixture of 1.00 g of 2-hydroxy-5-methylazobenzene, 0.94 g of ethyl bromoacetate, and 1.0 g of potassium carbonate in 4.0 mL of DMF was stirred at 60 °C for 8 h and diluted with ether, followed by washing with dilute hydrochloric acid and water to separate an organic layer. After removing the solvent, a residual crystalline mass was dissolved in 20 mL of THF and treated with 0.52 g of potassium hydroxide in 1 mL of water under reflux for 2 h to yield 0.98 g of orange crystals of mp 108–109 °C after acidification with hydrochloric acid. Found: C, 66.65; H, 5.29; N, 10.30. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.63; H, 5.22; N, 10.36. ^{1}H-NMR ($CDCl_3$): δ 2.48 (s, 3H, Ar–H), 4.84 (s, 2H, $-CH_2COO-$), 7.10 (1H, d, aromatic H), 7.22 (1H, d, aromatic H), 7.4–8.05 (6H, m, aromatic H). λ_{max} (ϵ) in ethanol: 314 nm (1.65×10^4).

Surface Modification. To a 6.5-mL anhydrous hexane solution of an azobenzenecarboxylic acid (1.3×10^{-3} mol/dm^3) was added 40 mg of thionyl chloride, followed by heating at 80 °C for 3 h under stirring. After removing the solvent and thionyl chloride, a residue was dissolved in 5 mL of benzene and dried under reduced pressure. This procedure was repeated three times. The azobenzene acid chloride was dissolved in 100 mL of anhydrous hexane, 65 mg of dry pyridine was added, and the solution was used immediately for the surface modification as follows. A 3 wt % aqueous solution of PVA was filtered through a nylon membrane filter with a 0.2-μm pore size. A quartz plate (1 × 3 cm^2) was cleaned ultrasonically for 15 min in acetone, concentrated nitric acid, aqueous sodium bicarbonate solution, and deionized water and spin-coated with the purified PVA solution at 2000 rpm for 20 s. The plate covered with a PVA thin film of ca. 300-nm thickness was heated at 100 °C for 5 min and immersed in a hexane solution of the acid chloride at 25 °C. The plate was taken out, washed with chloroform, and exposed to a dry nitrogen stream. These procedures were carried out under a dry nitrogen atmosphere. The plate was finally dried at 60 °C for 10 min and subjected to electronic absorption measurement.

Solution Esterification of PVA. PVA (49.2 mg; polymerization degree = 500, saponification degree = 100%) was dissolved in 2 mL of DMF at 150 °C under magnetic stirring. The solution was stirred at 70 °C 3 h after addition of 546 mg of C6AzOC6sC10, 437 mg of pyridine, and 347 mg of picryl chloride as a dehydrating reagent.[9] Benzene (2.2 g) was added to the reaction mixture to dissolve a precipitate, followed by stirring for 15 h at 80 °C. After filtration, a filtrate was evaporated to give a residue which was treated with acetone. The orange material was dissolved in chloroform, and the solution was poured into methanol to separate a gummy product which weighed 434 mg. The content of the azo chromophore was determined by UV absorption to be 30% by means of the electronic absorption spectrum.

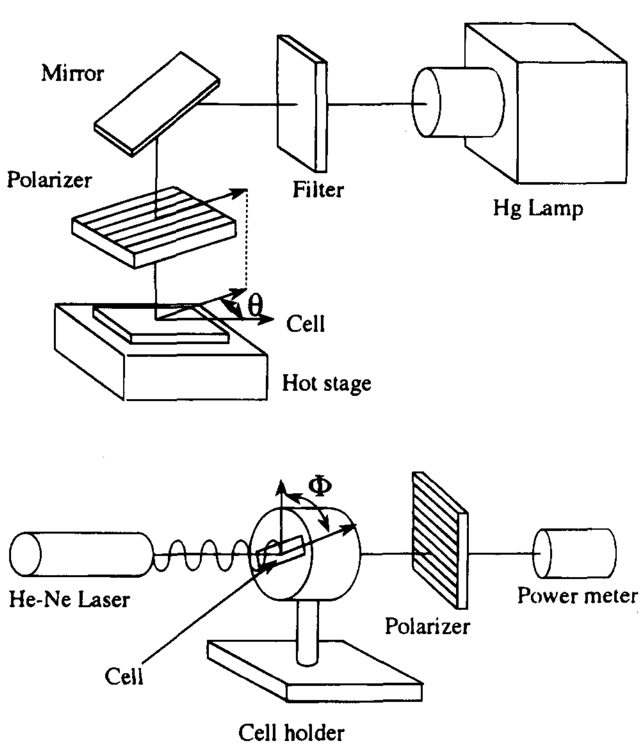


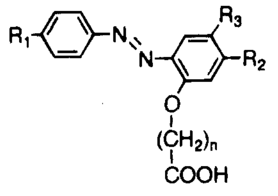
Figure 2. Experimental setup for the evaluation of photoinduced LC alignment.

Physical Measurements. UV absorption spectra were taken on a Hitachi 320. Atomic force microscopy (AFM) measurements were performed using a Seiko AFM300 of Seiko Electronics Co. at a scan speed of 100 μm/s. DSC measurement was made with a Seiko DSC 2000.

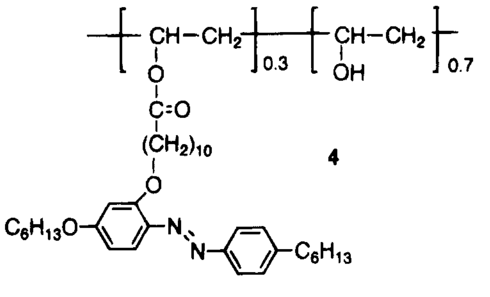
LC Cell Assemblage and Photobirefringence Observation. Two types of cell were fabricated with the use of azo-modified PVA plates. A nematic LC containing spherical glass spacers of 5 μm diameter was placed between an azo-modified plate and a quartz plate surface-modified with lecithin for a homeotropic alignment to make a hybrid-type cell. Another type of cell was constructed by sandwiching an LC between a couple of azo-modified plates. A cell was exposed to a 500-W high-pressure mercury arc through a filter (Toshiba Y-43; >430 nm) and a polarizer, similarly as in our previous papers. The LC alignment induced by the linearly polarized light was monitored by measuring the light intensity of a probing polarized He–Ne laser beam passed through the cell and a crossed analyzer as a function of the angle of a cell axis rotating around an optical axis.[5] Figure 2 shows the experimental setup for irradiation of a cell and birefringence measurement. An irradiation angle θ is an angle contained by a tentative cell axis and the direction of polarization of the actinic light, whereas the rotational angle ϕ of the cell is defined as an angle between the cell axis and the direction of the electric vector of a probing He–Ne laser beam.

Results and Discussion

Surface Modification. Our previous paper showed that treatment of PVA films with azobenzene acid chlorides in benzene leads to chemical modification of the surface and is useful to prepare the command surface to regulate the LC alignment between homeotropic and planar alignment upon alternate exposure to UV and visible light.[10] As an extension of this technique, azobenzenecarboxylic acids (**1**–**3**) were converted into acid chlorides using thionyl chloride for the esterification of surface hydroxyl (OH) groups of a PVA film. According to our previous paper,[10] a PVA-coated quartz plate was immersed in a benzene solution of the acid chloride having hexyl residues (**1**) in the presence of pyridine to introduce selectively the azobenzenes on the PVA surface. Electronic absorption measurement of the modified films showed that the amount of the azo chromophore was much larger than that attached specifically to the surface. In order to suppress the excessive reaction on the surface, the solvent was replaced by hexane to examine reaction conditions for the surface modification in more detail. The surface reaction was carried out under a dry nitrogen atmosphere to eliminate deterioration of a film surface during the reaction and subsequent washing with chloroform owing to the action of moisture which domages the surface during evaporation of chloroform. The surface-modified quartz plate using the acid chloride of C6AzO-C6sC10 (**1**) is designated plate-1, and those obtained using the acid chlorides of AzOC1sC10 (**2**) and AzOC1sC1 (**3**) are designated plate-2 and plate-3, respectively.



1 (C6AzOC6sC10) : R_1=C_6H_{13}, R_2=$C_6H_{13}O$, R_3=H, n= 10
2 (AzOC1sC10) : R_1=H, R_2=H, R_3=CH_3, n=10
3 (AzOC1sC1) : R_1=H, R_2=H, R_3=CH_3, n=1



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The amount of azobenzene units introduced on a polymer surface was evaluated from the absorbance at the absorption maximum of the surface-treated film assuming that the absorption coefficient is not affected by attachment of the chromophore to the surface. Absorbances at an early stage of the reaction contain an error within 10% owing to their low values. The density was expressed as the number of chromophores per 1 nm^2. Its dependence on reaction time is illustrated in Figure 3. In the cases of plate-1 (Figure 3a) and plate-2 (Figure 3b), the average density values leveled off in the range of 2−4 OH groups/nm^2 before about 60 min. This suggests that the azobenzenes are selectively introduced on the film surface of PVA in the plateau region. When the reaction time exceeded 60 min, an increase in the average density was observed again. This may be due to further esterification of inner OH groups. As the reaction proceeds, an acylated segment becomes compatible with the solvent molecules to lead the inner OH groups to be exposed to the reaction medium. This situation takes place markedly in the case of the esterification of a film of the partially saponified PVA with AzOC6sC10. Films of PVA with a 80% saponification degree displayed larger density values of the azo group than those of 100% saponified PVA, indicating an increased reactivity because of a reduction of the hydrogen bond network.

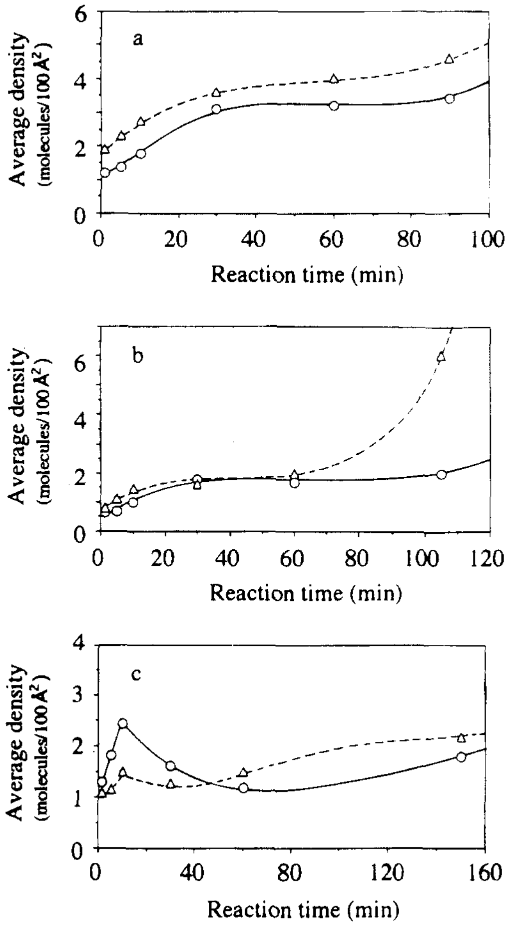

Figure 3. Surface esterification of fully saponified (○, full lines) and partially saponified (△, dotted lines) PVA films with (a) C6AzOC6sC10, (b) AzOC1sC10, and (c) AzOC1sC1, respectively.

Ikada and Matsunaga estimated the density of OH groups of PVA on a solid film by employing the surface-selective carbamoylation with an isocyanate, followed by hydrolysis to yield an amine which was analyzed by a fluorescent probe technique.[11] According to their technique, an average area occupied by a hydroxyl group directly exposed on a PVA surface was determined to be 0.37 nm^2 which is equivalent to 2.7 OH groups per nm^2. Although the saponification degree of the PVA was not specified in their report, the value agrees reasonably with our results. The PVA surface has 5.3 OH groups per 1 nm^2 assuming that every OH group orients in the same direction. The smaller OH density in our observation suggests that esterification with the acid chlorides derived from **1** and **2** occurs specifically at the uppermost surface of PVA films to offer a novel way to surface-selective modification.

In the case of plate-3, an abrupt increase in the average density was observed at an early stage of the reaction, followed by an anomalous decrease in the density (Figure 3c). This behavior is more remarkable for a partially saponified PVA film. No plateau value of the average density was found during this reaction. This was confirmed by AFM measurements which indicated that no essential deterioration took place on a film surface of partially or fully saponified PVA even after the surface treatment for 60 min when the acid chloride of C6AzOC6sC10 was employed (Figure 4a). On

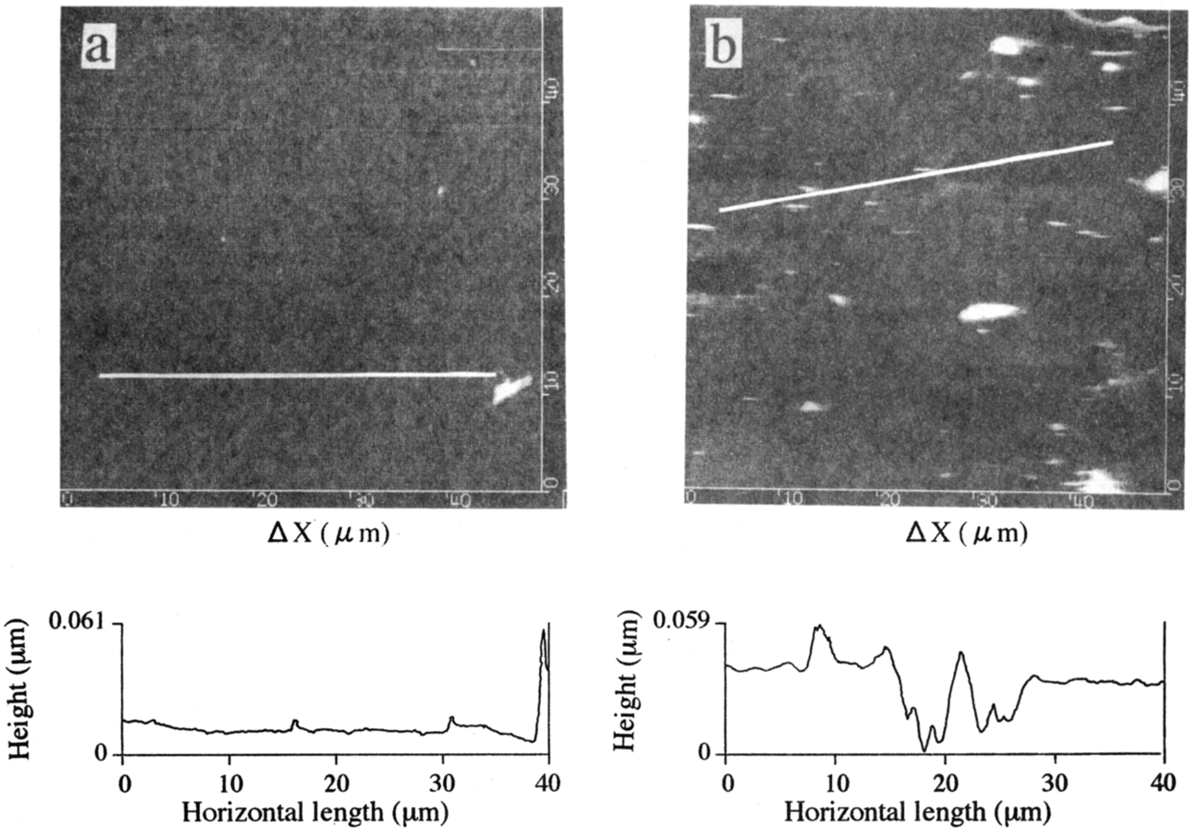

Figure 4. Atomic force microscopy measurements of PVA film surfaces reacted with (a) C6AzOC6sC10 and with (b) AzOC1sC1.

the contrary, the reaction of a thin film of fully saponified PVA with AzOC1sC1 resulted in impairment of surface flatness after 60 min although no marked damage was observed at an early stage of the surface esterification. In particular, a film surface of the partially saponified PVA suffered from severe destruction of the flatness leading to the formation of craters with a diameter of several microns and a depth of about 20 nm, as given in Figure 4b. This might be due to the partial dissolution of the surface-modified polymer in chloroform during the washing. The progress of the reaction weakens the hydrogen bonds of the PVA network so that the resistance to the organic solvent is reduced to enhance the solubility of the polymer.

The different behavior between plate-1 or plate-2 and plate-3 may arise from the higher reactivity of the acid chloride of **3**. The electron-withdrawing substituent of an alkoxy group at the α-carbon atom of the acid chloride activates the reactivity when compared with the acid chlorides of **1** and **2** having long alkyl chains.

Alignment Photocontrol. Irradiation of the azobenzene moieties on substrate surfaces with blue light of wavelengths longer than ca. 400 nm for the n,π^*-excitation affords a photostationary state containing a trans isomer as a major component and causes the uniaxial reorientation of the chromophore to result in a homogeneous alignment of nematic LC when an azo-modified substrate plate is used to fabricate an LC cell.[5,6] This type of photoinduced in-plane LC alignment is enhanced by heating a cell above the nematic/isotropic transition temperature (T_{NI}). A hybrid cell with NPC-02/5CB was assembled with a plate (plate-1) covered with a PVA film surface modified with **1** and irradiated with linearly polarized light of wavelengths longer than 400 nm at 40 °C above T_{NI}. Weak birefringence in liquid crystal cells was observed in some cases even before photoirradiation, as illustrated in Figure 5b. This may be due to the so-called flow-induced alignment of the liquid crystal phase during the cell assembly. Polarized photoirradiation was carried out at various irradiation angles (θ) which are defined in Figure 2. The exposed cell was subjected to monitoring the photoinduced birefringence due to the in-plane uniaxial orientation of the LC layer by measuring the transmittance of a probing polarized laser beam at room temperature. As shown in Figure 5a, there appeared peaks with maximum transmittance (T_{max}) and valleys with minimum transmittance (T_{min}) at a regular 90° separation, indicating a photoinduced homogeneous alignment of the mesophasic layer. This is so since the transmittance (T) is related to ϕ when probing light of wavelength λ is passed through a cell of a gap d, filled in with an LC of birefringence Δn, by

$$T = \sin^2 2\phi \sin^2(\pi d \Delta n/\lambda)$$

Rotational angles displaying minimum transmittances appear approximately at $\theta + \pi/4 + n(\pi/2)$, confirming that the alignment direction of the irradiated cell is roughly perpendicular to the polarization plane of the light.

In stark contrast to the results, only immature homogeneous alignment was observed upon the polarized irradiation when a cell was fabricated with a plate-2 modified with AzOC1sC10 (Figure 5b). AzOC1sC1 having a shorter spacer linking the azo chromophore on the polymeric surface (plate-3) demonstrated no aligning ability, as illustrated in Figure 5c. These results suggest strongly that the photoregularity is influenced by both spacer length and alkyl substituent. In particular, the molecular shape of the photochromic moiety substituted with hexyl residues on both ends of the chromophore plays a critical role in the azimuthal alignment photocontrol; C6AzOC6sC10 gave

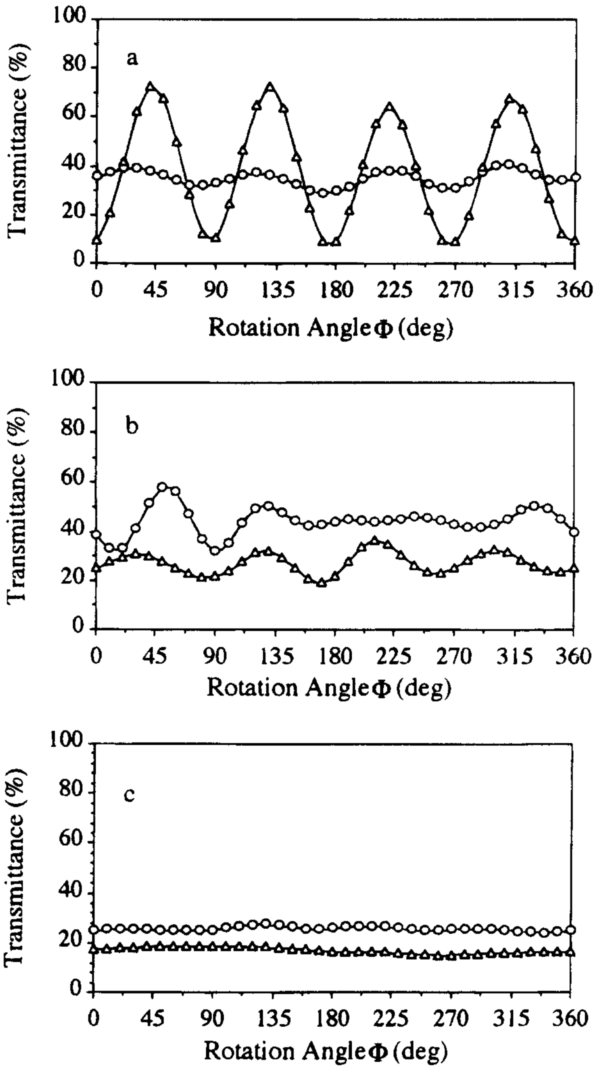

Figure 5. Angular dependence of transmittance of a monitoring He–Ne laser beam (633 nm) through an LC (NPC-02/5CB) cell fabricated with (a) plate-1 modified with C6AzOC6sC10, (b) plate-2 modified with AzOC1sC10, and (c) plate-3 modified with AzOC1sC1 upon the rotation angle of the cell before (○) and after (△) exposure to polarized visible light (>400 nm).

a much better result than AzOC6sC10 with the same spacer did.

As shown previously, the photoinduced in-plane reorientation of nematic LC takes place with difficulty when a cell made from an azo-modified silica plate is exposed to polarized light at temperatures below T_{NI}.[5,6] A similar behavior was observed for the hybrid cell; no photoinduced birefringence of the mesophasic layer was detected even after prolonged irradiation at room temperature. This shows that the molecular motion at the boundary region below T_{NI} is restricted[12,13] possibly because of the formation of molecular aggregates with a higher order which behave like a smectic phase on a substrate surface.[14]

The efficiency of the LC alignment induced by polarized light irradiation was also influenced by the nature of nematic LCs. The nematic LCs shown in Figure 1 were filled in a cell assembled with a couple of the PVA plates azo-modified with 1, respectively, to determine the photoalignment at temperatures above their T_{NI}. Although our previous work disclosed that the in-plane reorientation of DON-103 takes place with great ease above its T_{NI} upon polarized irradiation of silica substrate surface-modified with laterally attached azobenzene groups to give photoimages with a high resolution,[5] the homogeneous alignment was incomplete even after prolonged irradiation at 75 °C. A contrast defined as T_{max}/T_{min} was employed here as a measure of the photoalignment efficiency for further discussion and summarized in Table 1. The alignment efficiency was lower also for 5CB itself. Furthermore, the photoinduced alignment of DON-103 was frozen-in on storage for a while in the dark and not altered any longer by the polarized light irradiation with a different electric vector. This implies that the liquid crystal molecules are adsorbed firmly on the PVA surface and are prevented from reorientation.

Table 1. Contrast Values Defined as T_{max}/T_{min} of Cells Filled with Various LCs

LC	contrast	LC	contrast
DON-103	2.1	5CB	2.7
NPC-02	3.2	NPCO2/5CB	9.6

Our recent paper showed that the uniaxial alignment of LC is brought about by assembling an LC cell with a substrate plate covered with a thin film of poly[(4-methacryloyloxy)azobenzene] (pMAz) which is exposed to polarized light for the n,π*-transition of pendent azobenzene residues before the cell fabrication.[15] The alignment disappeared gradually on standing even in the dark possibly owing to the compatibility of LC with the polymer enhancing the thermal randomization of the photoinduced orientation of azobenzene chromophores in the polymer matrix. The stability of the photoinduced alignment presented here contrasts with the result for pMAz and must result from the incompatibility of hydrophilic PVA and LCs. In order to confirm the effect of affinity of azo-modified polymer with LC on the photoalignment stability, PVA was esterified with the azobenzenecarboxylic acid (**1**) to give a polymer substituted with azobenzene residues (**4**: PVA-Az). The degree of esterification was about 30%, and the polymer was tacky and showed no glass transition above room temperature. Although a thin film of PVA-Az coated on a plate was irradiated with the polarized actinic light, no reorientation of LC molecules was brought about when an LC cell was fabricated using the exposed plate. This may arise from the rapid randomization of photoinduced orientation of azo chromophores because of the segmental motion of the polymer with a lower T_g. Closely related work revealed that a uniaxial orientation of azobenzene chromophores attached to a liquid crystal polymeric backbone decreases drastically on heating a polymer layer above the transition temperature.[16]

As mentioned above, when the surface esterification of a PVA film is carried out in benzene, the introduction of azobenzene units takes place more efficiently and is not restricted to the uppermost surface layer of the film to yield a film grafted with azo-modified chains. It was observed that this type of a PVA film modified with an excess of the azo groups displays no in-plane LC reorientation under illumination with linearly polarized visible light. The lack of alignment photoregulation is caused by the ease in the molecular motion of the azo chromophores bound on the surface layer of a PVA film in a manner quite similar to the case of PVA-Az. The failure to the in-plane alignment photoregulation with a film of the PVA substituted with azo chromophores as well as a PVA film modified with an excess of azobenzenes contrasts sharply with our previous results; the out-of-plane alignment between homeotropic and planar modes is successfully achieved with use of a thin film of PVA bearing azobenzenes in the side chain and a PVA film surface-modified with azo chromophores upon alternate photoisomerization with UV and visible light.[17] This reflects the difference in the sensitivity of commanding ability of polymeric surfaces between the in-plane and the out-of-plane alignment regulations. Systematic studies have been so far carried out on polymeric Langmuir–Blodgett (LB) membranes regulating both the in-plane and out-of-plane LC alignment.[18] Although the out-of-plane regulation is achieved by alternate exposure to UV light to give the cis isomer as a major component in a photostationary state, the azimuthal photocontrol of LC orientation is demonstrated specifically by a single monolayered LB membrane exposed to linearly polarized UV light. A multilayered LB membrane has no ability to command the in-plane alignment regulation, whereas the out-of-plane alignment is performed by the multilayered membrane when irradiated with alternate UV and visible light. All these observations indicate that the introduction of azo chromophores specifically onto an uppermost surface of a polymeric film leads to an azimuthal alignment photocontrol of LCs.

Since surface-selective modification of the side-on type azobenzene residues gives rise to a persistent photoinduced LC alignment, the photoregulation of the azimuthal reorientation of LC (NPC-02/5CB) molecules filled in a cell was achieved by changing the direction of polarization plane of the actinic light. The cell was illuminated first with polarized light at $\theta = 0°$, followed by irradiation with the same light after rotating the polarization plane angle at $\theta = 30°$ and $60°$, respectively. The results show the parallel shift of the curve reflecting the birefringence of the mesophase and confirm that the reorientation of the LC is readily photoregulated in a way similar to the case of the azo-modified silica plates.[5] This suggests that the reversible photoregulation of azimuthal LC alignment may be achieved by polymer films which are modified at their surfaces with photoactive molecules as molecular rotors.

It should be stressed that the extent of the uniaxial orientation evaluated according to the experimental setup shown in Figure 1 is based on the measurement of an averaged transmittance in an area determined by a diameter of a monitoring laser beam. Actually, polarized microscopy observations revealed that the present photoaligned LC cells do not always possess good optical quality owing to the imperfect uniformity of the uniaxial alignment and the appearance of disclination. The former arises probably from the lack of homogeneity of the density and the distribution of the azobenzene group tethered on a substrate surface according to the present procedure since the LC alignment itself reflects the molecular aspects of a substrate surface. The latter may be due to insufficient anchoring strength of the present command surface. Further efforts are needed to overcome these problems.

Conclusion

The introduction of azobenzene groups specifically on a surface of a PVA thin film is a prerequisite for the in-plane alignment regulation with linearly polarized visible light for the n,π^*-excitation of the chromophores. Selectivity of the surface modification was influenced particularly by the solvent, structure of acylating reagents, and saponification degree of PVA. The surface esterification of a PVA film carried out under optimized reaction conditions resulted in the attachment of photoisomerizable units specifically on hydroxyl groups localized on a film surface to afford an average density of 2–3 units per 1 nm^2. The azo-modified PVA films act as a command surface to regulate azimuthal LC alignment by the action of linearly polarized light. The molecular structure of an azobenzene moiety plays a critical role in the photoregulation; an azobenzene substituted with hexyl residues at both p-positions acts as a molecular rotor to achieve the in-plane photoalignment regulation, whereas no photocontrol was obtained by azobenzene without long alkyl substituents.

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