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Photogeneration of pretilt angles of nematic liquid crystals by azobenzene-containing monolayers on poly(acrylic acid) films

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A convenient procedure to fabricate azobenzene-containing monolayers capable of performing the photoalignment of nematic liquid crystals (LCs) with pretilt angles has been elaborated. The photoactive monolayers were readily prepared by the surface-selective adsorption of *p*-butylazobenzene substituted with an ω-aminoalkyl residue to the outermost surface of a poly(acrylic acid) thin film. After the fabrication of an LC cell, the monolayers generated homeotropic LC orientation, which was transformed into homogeneous alignment with tilting angles by oblique irradiation with non-polarized UV light. The azimuthal direction of the photoinduced LC alignment was consistent with the propagation direction of the UV light, suggesting that the LC photoalignment results from direction-selective *E* to *Z* photoisomerization leading to re-orientation of the azobenzene chromophores. The photogenerated pretilt angles of LC alignment were significantly dependent on the dielectric anisotropy of LC and the surface density of the azobenzene in the monolayers.

Introduction

The surface-assisted control of nematic liquid crystal (LC) alignment utilizing photochemical reactions of outermost molecular as well as polymeric layers on substrate surfaces is attracting current attention from practical viewpoints because of its versatile practical applicability to light-driven LC displays, optical memory media, optical elements and so forth.[1] The first observation of photoinduced LC alignment alteration between homeotropic and random planar states was made by employing *E*/*Z* photoisomerization of azobenzene chromophores tethered to a silica surface, which was referred to as a command surface or layer.[2] This work was followed by the illumination of the command surfaces with linearly polarized light to give rise to homogeneous alignment with azimuthally uniaxial LC orientation which can be induced by using thin films of polymers exhibiting photoisomerization,[3–6] photocycloaddition[7,8] and photodecomposition.[9,10] It has been revealed that the LC alignment by photoirradiation with linearly polarized light is markedly influenced by the molecular structures as well as the levels of anisotropic orientation of photo-reactive chromophores.[2–12]

Current interest has been concentrated on developing materials and procedures to generate and manipulate pretilt angles of nematic LCs by photochemical processes because the precise control of pretilt angles is one of the important requirements in manufacturing nematic LC displays such as twisted and vertical alignment (VA).[11,13,14] The spatial orientation of an LC director is defined by a polar angle (α), *i.e.* pretilt angle, and an azimuthal angle (β), as indicated in Fig. 1. It was found that the continuous alteration of pretilt angles of nematic LC molecules from homeotropic alignment to homogeneous is attained by oblique photoirradiation of an LC cell, whose inside walls are modified with thin films of azobenzene-containing polymers, even when the light was not linearly polarized.[15,16] To our knowledge, this was the first generation of LC pretilt angles by photochemical transformation of outermost layers on substrate surfaces. The mechanism of this kind of three-dimensional LC photocontrol has been revealed experimentally. Oblique photoirradiation of thin films of amorphous[17] or liquid crystalline[18] polymers incorporating azobenzene side chains with non-polarized light results in the three-dimensional control of molecular orientation of azobenzenes in such a way that the long axis of the molecules orients in parallel with the propagation direction of the incident light. Taking notice of the ease in the generation of pretilt angles by using azobenzene-containing polymers, we have carried out systematic investigation on the photogeneration of LC pretilt angles by using poly(methacrylates) with azobenzene side chains with various kinds of *para*-substituents.[19] Furthermore, we have reported recently that a polymer with *p*-trifluoromethoxyazobenzene side chains induces the generation of high pretilt angles of nematic LCs by slantwise photoirradiation and is applicable to fabricate VA cells.[20] The photoirradiation with non-polarized light determines the three-dimensional orientation of a nematic LC even though LC is doped in polymer networks with tethering azobenzene side chains.[21] Whereas the three-dimensional photocontrol of LCs has been achieved in these ways, we have insufficient information concerning the mechanism of the photogeneration of pretilt angles and the relationship between pretilt angles and the nature of nematic LC molecules.

We reported previously a convenient method to prepare LC-photoaligning monolayers formed by the surface-selective adsorption of an azobenzene derivative possessing an aminoalkyl residue on a thin film of poly(acrylic acid), aiming at the achievement of LC photoalignment by irradiation with linearly polarized light.[22] This procedure has the following advantages in the preparation of command surfaces. First, the preparative procedure is quite simple and consists of the immersion of a

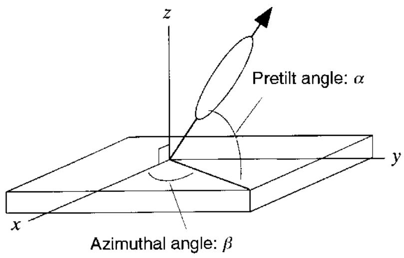

Fig. 1 Illustration of a tilted nematic liquid crystal on a substrate surface. Arrow indicates an orientational director of nematic LC molecules.

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substrate plate coated with a thin film of the polymer in a dilute solution of an ω-aminoalkylazobenzene to form a self-assembled monolayer. Second, the density of the azobenzene moieties in monolayers is readily controlled by the co-adsorption with photo-inactive long-chain alkylamine. Thirdly, self-assembled monolayers thus prepared provide a model system for LC-aligning polymer films because the monolayered azobenzene units are attached specifically to a topmost surface of a polymer film. We report herein the three-dimensional photocontrol of LC alignment by using this type of self-assembled monolayers upon oblique irradiation with non-polarized UV light, focusing on our effort to reveal that photogenerated pretilt angles are critically influenced by the nature of nematic LCs.

Experimental

Materials

Chemical structures of materials used in this study are shown in Fig. 2. Poly(acrylic acid) (pAA, $M_w = 2.5 \times 10^5$) was purchased from Aldrich. 4-(10-Aminodecyloxy)-4′-butylazobenzene (4AzA) was prepared according to our previous paper.[23] Octadecylamine (C18A) was obtained from Kanto Chemical Co. and used after purification by recrystallization from hexane. Two kinds of nematic LCs, consisting of a binary mixture of phenylcyclohexane derivatives, were kindly donated by Rodic Co. Ltd. One is a polar LC of RDP-60774 exhibiting a nematic–isotropic phase transition temperature (T_{NI}) = 42.6 °C, optical anisotropy (Δn) = 0.139, refractive index (n_0) = 1.501 and dielectric anisotropy ($\Delta\varepsilon$) = 11.8. Another is a less polar LC of NPC-02 exhibiting $T_{NI} = 35.0$ °C, $\Delta n = 0.075$, $n_0 = 1.489$ and $\Delta\varepsilon = -0.1$. A dichroic diaminoanthraquinone dye, LCD-118, donated by Nippon Kayaku Co., Ltd., was dissolved in the nematic LCs for the determination of the azimuthal direction of LCs.[24]

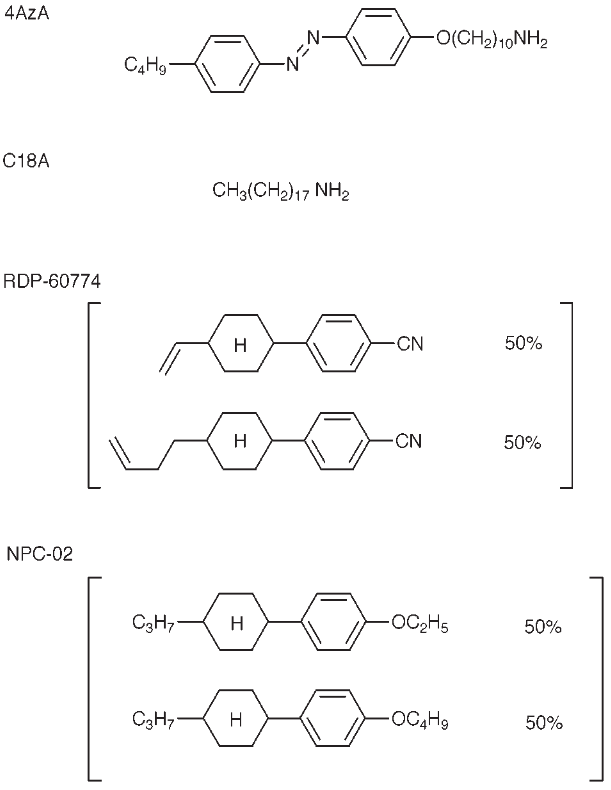

Fig. 2 Chemical structures of materials employed in this study.

Slantwise irradiation of LC cells

The preparation of azobenzene monolayers was performed according to our previous paper.[22] The photoactive monolayer modified with 4AzA (Az-pAA film) was prepared by the immersion of a spin-coated film of pAA on a quartz plate into a 2.5×10^{-5} mol dm^{-3} solution of 4AzA in hexane at 40 °C for 30 min, followed by rinsing with fresh hexane. The surface density of 4AzA in the photoreactive monolayers was tuned by the co-adsorption with C18A under the same conditions to give Az/C18A-pAA films. Three kinds of monolayers with different densities of the azobenzene (AD) of 0.6, 0.8 and 2.0 molecules nm^{-2} were prepared. An empty cell was assembled by glass plates covered with Az-pAA films or Az/C18A-pAA films and filled with a nematic LC above T_{NI} by a capillary force and cooled to room temperature. A cell gap was adjusted to be 25 μm by using two strips of poly(ethylene terephthalate) film spacers. An LC cell was irradiated obliquely with non-polarized 365 nm light which was obtained by passing light from a 200 W Hg–Xe lamp (San-ei Electric MFG. Co., Supercure-203S) through the combination of glass filters (Toshiba, UV-D36A and UV-35). The incident direction of the non-polarized UV light was set at 70° from a substrate plane of the cell as illustrated in Fig. 3(a). θ indicates the angle between the projection direction of light path and an axis of the LC cell.

Slantwise irradiation of films before cell assembly

A pair of the Az-pAA films with AD = 2.0 molecules nm^{-2} were irradiated obliquely with UV light at an exposure dose of 1.0 J cm^{-2}. Subsequently, an antiparallel empty cell was fabricated and filled with the nematic LC containing the dichroic dye. The evaluation of cell properties was performed in the same manner to that described previously.[22]

Pretilt angle measurements of LCs

Photogenerated pretilt angles of LCs were determined by the crystal rotation method.[26] A polarization-modulated transmission ellipsometer (JACSO, BFA-150)[27,28] equipped with an He–Ne laser beam and a photoelastic modulator (PEM) operating at a modulation frequency of 50 kHz was used. Two parameters, phase difference angle (Δ) and relative amplitude ratio (Ψ), for an LC cell were measured when the LC cell was rotated from −60° to 60°, as shown in Fig. 3(b). Pretilt angles were calculated from these parameters.

Results and discussion

Azimuthal orientation of LCs by slantwise UV irradiation

Azobenzene-containing monolayers were prepared readily by the chemisorption of 4-(10-aminodecyloxy)-4′-butylazobenzene (4AzA) on a spin-coated film of poly(acrylic acid) (pAA) through NH_2–COOH interaction and used for LC photoalignment experiments. Homeotropic LC alignment was spontaneously induced for both LCs, RDP-60774 and NPC-02, when LC cells were assembled by glass plates covered with the

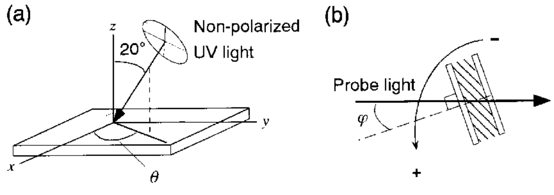

Fig. 3 Schematic presentation of (a) slantwise non-polarized light irradiation system and (b) experimental set-up for pretilt angle measurement of nematic LCs. φ indicates the incident angle of probe light with respect to the LC cell.

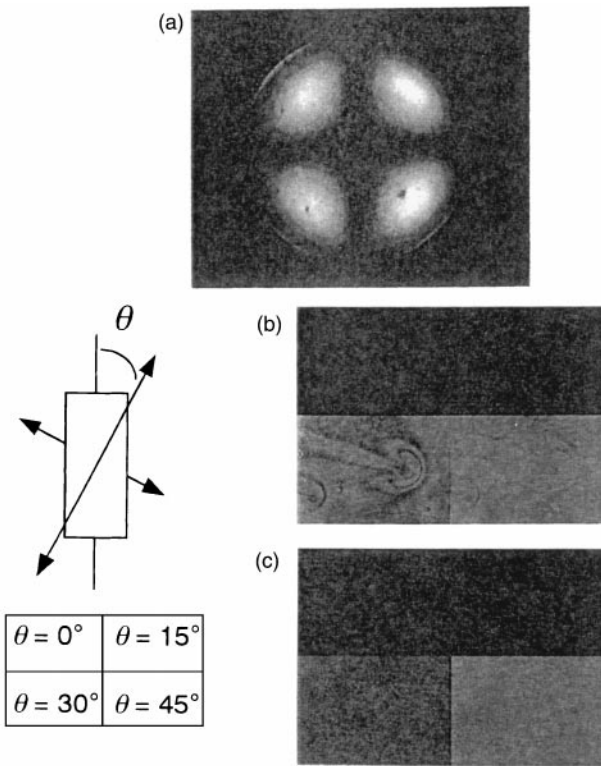

Fig. 4 Conoscopic interference image (a) and polarized micrographs (b, c) of an LC cell fabricated with 4AzA/C18A-pAA films (AD = 0.8 molecules nm^{-2}). The arrows indicate the direction of the optical axes of polarizers in the polarized microscope. (a) Initial homeotropically aligned LC cell; (b) LC cell after irradiation at 100 mJ cm^{-2}; (c) tilting aligned LC cell in a photostationary state.

azobenzene-modified pAA film, as revealed by conoscopic interference images presented in Fig. 4(a). When an LC cell prepared by Az-pAA films with AD = 2.0 molecules nm^{-2} was subjected to slantwise irradiation with non-polarized 365 nm light the homeotropic alignment began to tilt and finally gave rise to homogeneous alignment through the continuous transformation of aligning states of LC molecules. Fig. 4(c) shows the optical texture of the LC cell after UV irradiation of approximately 400 mJ cm^{-2} to give a photostationary state of *E*/*Z* photoisomerization, suggesting that the homogeneous alignment exhibits a mono-domain texture with excellent optical quality. The azimuthal direction of the photoinduced homogeneous alignment was determined by measuring the dichroism of a guest dye doped in the nematic LC. Fig. 5 shows a circular diagram of polarized absorbances of the dichroic dye at 633 nm as a function of angle between the polarization plane of a probing He–Ne laser beam and the incident plane of non-polarized light, indicating that the azimuthal director of nematic LC is parallel to the propagation plane of the light. A dichroic ratio, $A_{\max}:A_{\min}$, of approximately 4.0 : 1.0 observed for the obliquely photoirradiated cell was in agreement with that for an LC cell irradiated with linearly polarized UV light from the surface normal,[22] revealing that photoirradiation even with non-polarized light leads to the emergence of a Weigert effect which is observed conventionally by irradiation with linearly polarized light.[29]

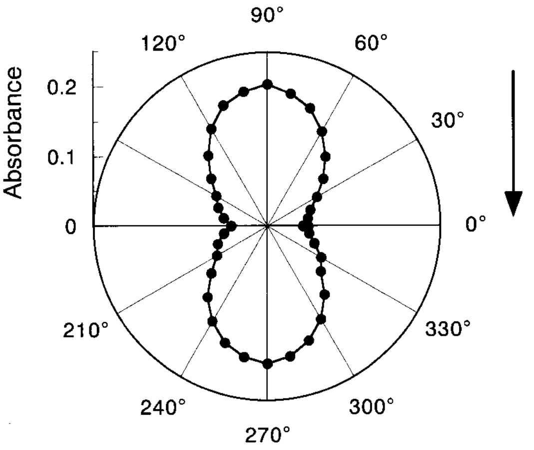

Fig. 5 Circular diagram of absorbances at 633 nm observed for a dichroic dye-doped LC cell whose inside walls were modified with 4AzA-pAA films (AD = 2.0 molecules nm^{-2}). The arrow corresponds to the incident plane of the non-polarized UV light.

The photoinduced azimuthal re-orientation of LC molecules can be interpreted as a result of the allowed and forbidden photochemistry of the azobenzene chromophore. The azobenzene residues absorb photons when non-polarized 365 nm light is perpendicular to the transition moment of the chromophore, resulting in *E* to *Z* photoisomerization. On the other hand, the azobenzene residues do not absorb the light when their transition moment lies parallel to the propagation direction of the light. The repetition of photoisomerization results in re-orientation of the *Z* isomer of the azobenzene moieties in such a way that the molecular axis orients parallel to the propagation direction of the incident light. It follows that homogeneous alignment with the orientational direction in line with the propagation plane of the light is obtained since the *Z* isomer induces the planar orientation of LCs. Consequently, the present results reveal that re-orientation of azobenzene moieties takes place upon slantwise irradiation with non-polarized 365 nm light even though the chromophore is tethered to the outermost surface of a substrate plate. Attempts to observe photoinduced dichroism of a 4AzA-pAA monolayer upon slantwise irradiation with non-polarized light at 365 nm were unsuccessful due to the intrinsically weak absorbance (*ca.* 0.008) of the azobenzene residues in the monolayers.[22]

Photogenerated pretilt angles of nematic LCs upon slantwise photoirradiation

Precise changes in pretilt angles during the photoinduced LC alignment upon slantwise irradiation were followed by the crystal rotation method. AD of 4AzA in monolayers was controlled by co-adsorption with octadecylamine (C18A). Three kinds of photoactive monolayers with AD = 0.6, 0.8 and 2.0 molecules nm^{-2} were employed to investigate the effect of the surface density of the azobenzene moieties on the photocontrol of pretilt angles. Fig. 6 shows crystal rotation signals observed for an LC cell of RDP-60774 fabricated with a photoactive monolayer with AD = 0.8 molecules nm^{-2} upon slantwise irradiation with non-polarized UV light. The crystal rotation signals correspond to three-dimensional birefringence of the nematic LC cell as a function of the incident angle $\varphi = 0°$ which suggests that the LC alignment is uniaxially homeotropic with a pretilt angle of *ca.* 90° [Fig. 6(a)]. This changed to an inclined homeotropic alignment with a pretilt angle of 87° at an exposure energy of 80 mJ cm^{-2} when the incident angle of the actinic light was 20° from the surface normal [Fig. 3(a)]. As shown in Fig. 6(b), the crystal rotation signals are shifted to the propagation direction of the actinic light and exhibit an asymmetric sin Δ curve with respect to $\varphi = 0°$. The photoinduced pretilt angle levelled off at a pretilt angle of *ca.* 30°, which was calculated from the experimental data shown in Fig. 6(c) at exposure doses of 150 mJ cm^{-2} or more. Polarized optical microscope observation of the LC cell revealed that the tilted alignment displays excellent optical quality without any reverse tilt, in contrast to a photoaligned LC cell prepared by linearly polarized light irradiation. Transient pretilt angles of the polar LC of RDP-60774 in the range $30° < \alpha < 80°$ were not measurable because of the deterioration of the nematic LC

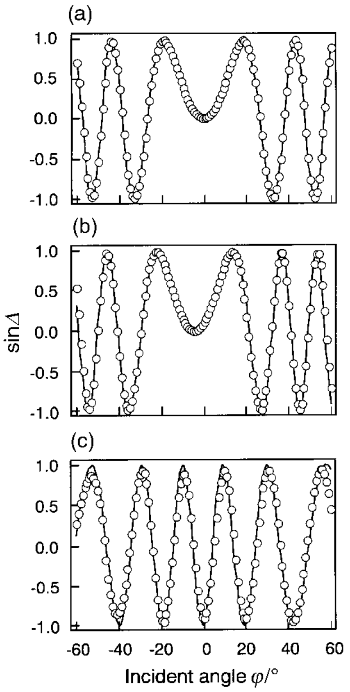

Fig. 6 Crystal rotation signals (a) in the initial state, (b) after slantwise irradiation with non-polarized UV light at 80 mJ cm^{-2}, and (c) in a photostationary state as a function of incident angle φ of the probing light. The LC cell of RDP-60774 was fabricated with 4AzA/C18A-pAA films (AD = 0.8 molecules nm^{-2}). Open circles: experimental data. Solid line: theoretical curve.

layer as shown in Fig. 4(b). Similar deterioration behavior of LC alignment was also observed for LC cells fabricated with spin-coated films of azobenzene-containing polymers.[17]

Fig. 7 shows pretilt angle changes of two kinds of nematic LCs of non-polar NPC-02 and polar RDP-60774 upon slantwise irradiation with non-polarized UV light. The circles, squares and triangles correspond to pretilt angles of LC in cells comprised of photoactive monolayers possessing AD = 2.0, 0.8 and 0.6 molecules nm^{-2}, respectively. It is worth mentioning that the average density of azobenzene residues in the photoactive monolayers determines critically the photocontrollability for three-dimensional LC alignment. For both nematic LCs, while an LC cell fabricated with photoactive monolayers possessing AD = 0.8 or 2.0 molecules nm^{-2} displayed photochemical control of LC alignments, no change from the initial homeotropic alignment was induced when AD < 0.6 molecules nm^{-2}. It should be stressed that photoinduced polar angles are significantly influenced by the surface density of the photoactive azobenzene residues, as observed for the polar LC, RDP-60774. 4AzA/C18-pAA films with AD = 0.8 molecules nm^{-2} generated a polar angle of 30.0 ± 0.5° at a photostationary state of E to Z photoisomerization of the azobenzene units, while those with AD = 2.0 molecules nm^{-2} gave rise to homogeneous alignment with a polar angle of about 0.1°. For LC cells filled with non-polar NPC-02, slantwise exposure doses of more than 100 mJ cm^{-2} resulted in no generation of polar angle of LC orientation, indicating that the dielectric anisotropy of LC molecules is also important for the photogeneration of pretilt angles. Consequently, the photoinduced tilted alignment was markedly affected by both the AD of photoactive azobenzene chromophores at the outermost surface and the dielectric anisotropy of LCs. These results suggest that intermolecular interactions between LC molecules and photoresponsive molecules at the interfacial region play an important role as driving forces for the photogeneration of pretilt angles of nematic LCs.

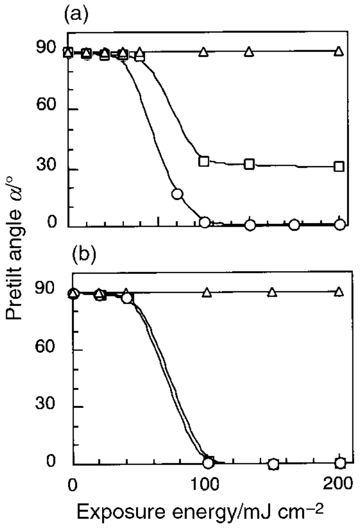

Fig. 7 Pretilt angle changes of (a) RDP-60774 and (b) NPC-02 as a function of exposure energies of non-polarized light at 365 nm. Photoalignment layers in LC cells have different surface densities of 4AzA (circles, AD = 2.0 molecules nm^{-2}; squares, AD = 0.8 molecules nm^{-2}; triangles, AD = 0.6 molecules nm^{-2}).

Azimuthal re-orientation of nematic LCs by slantwise photoirradiation

Azimuthal re-orientation of nematic LC molecules driven by the alternation of the polarization plane of linearly polarized light has been presented in our previous papers.[4,30,31] A plausible mechanism is as follows. As a result of two-dimensional photo-selection, azobenzene moieties with a transition moment in parallel with the polarization plane of the actinic light photoisomerize preferably, resulting in re-orientation of the molecular axis perpendicular to the polarization plane of the actinic light.[32] Subsequently, nematic LC molecules surrounding the re-orientated azobenzene moieties alter their molecular orientation. On the other hand, slantwise irradiation with non-polarized UV light led to homogeneous LC alignment, the azimuthal angle of which is parallel with the incident plane of the actinic light. We investigated the re-orientation behavior of the photoaligned LC molecules by changing the incident angle (θ) of the actinic light upon slantwise irradiation. Fig. 8 shows the angular dependence of a probing He–Ne laser beam through the LC cell and an analyzer. An LC cell of NPC-02 was fabricated with 4AzA-pAA films with AD = 2.0 molecules nm^{-2}. The maximum transmittance corresponding to the direction of the

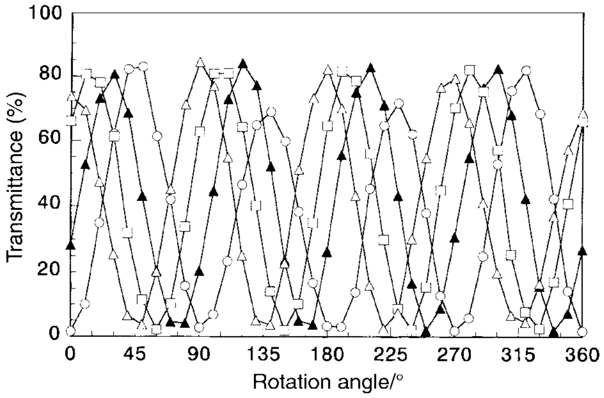

Fig. 8 Angular dependence of polarizing transmittance of a He–Ne laser beam at 633 nm passed through the tilted aligned LC cell and a crossed polarizer. The cell was obliquely exposed to non-polarized UV light with an incident angle (θ) of 0° (open circles), 15° (closed triangles), 30° (open squares) and 45° (open triangles), respectively.

incident angle (θ) of the non-polarized UV light was observed, and peaks of the maximum transmittance appeared at rotation angles of $\theta + 90^\circ \times n$. These results show that the re-orientation of the aligned LC molecules can be induced by slantwise irradiation with non-polarized UV light leading to photoalignment of azobenzene moieties at the outermost surface of the monolayer.

Conclusion

We have developed a simple procedure to fabricate self-assembled monolayers of an azobenzene derivative on an amorphous polymer film for the pretilt angle photocontrol of nematic liquid crystals as an interface model between the photoaligning layer and nematic liquid crystal. Slantwise irradiation with non-polarized UV light gives rise to orientational changes of nematic liquid crystals from homeotropic to tilted alignment, whose direction is parallel with the propagation director of the actinic light. Furthermore, the azimuthal direction of liquid crystal alignment is controllable by changing the propagation of the incident light. Three-dimensional alignment of liquid crystals is markedly dependent upon the surface density of the azobenzene and the dielectric anisotropy of the liquid crystals.

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