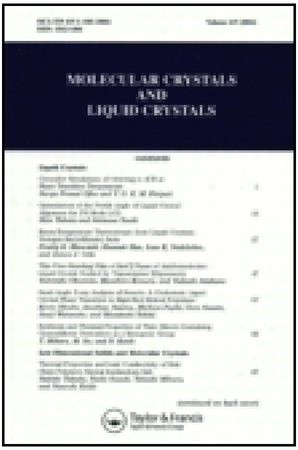

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Photocontrol of Alignment of Liquid-Crystalline Molecules in Photoresponsive Polymer Networks

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Photocontrol of Alignment of Liquid-Crystalline Molecules in Photoresponsive Polymer Networks

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A novel composite system consisting of a low-mass nematic liquid crystal and a crosslinked polymer with azobenzene side chains exhibited large birefringence upon irradiation with linearly polarized light. The extent of photogenerated birefringence depended on *p*-substituents and alkylene spacer lengths of the azobenzenes. Three-dimensional orientation of liquid-crystalline molecules was also induced by slantwise irradiation with non-polarized light in this composite system. Rewritable photopatterning exhibiting good storage stability was carried out by slantwise irradiation with non-polarized visible light.

Keywords: photoresponsive; polymer network; liquid crystal; birefringence; three-dimensional alignment

INTRODUCTION

The generation of optical anisotropy by photoirradiation has been attracting interest because of the capability of practical applications to optical elements and devices. Azobenzenes are commonly used as photoresponsive molecules to generate dichroism as a result of the reorientation of their molecular axis upon irradiation with linearly polarized light.[1] The photochromic molecules have been doped physically in poly(vinyl alcohol) (PVA)[2] or attached covalently to amorphous[3] and liquid-crystalline[4] polymer backbones to create photoinduced birefringent media. When an azobenzene is tethered to a surface layer of a substrate plate to assemble a cell filled with a nematic liquid crystal (LC), the alignment of LC is achievable as a result of the marked amplification of photoinduced orientational as well as structural changes of the surface azobenzene.[5] Homogeneous alignment of LC molecules is obtained by this kind of command layers, when actinic light is linearly polarized. In this case, the orientational direction of LC molecules is determined by the electric field vector of the light. It was also reported that the surface-assisted orientational direction of a nematic LC is determined specifically by the incident direction of non-polarized light.[6,7] In connection with the elucidation of the photoalignment mechanism by using non-polarized light, we have revealed that azobenzene residues tethered to amorphous[8] as well as liquid-crystalline[9] polymer backbones tilt to the direction in line with the propagation direction of non-polarized light. This procedure has been applied to control pretilt angles of LCs, which are filled in cells assembled with substrate plates covered with azobenzene polymer ultrathin films.[8,10] The surface-assisted photocontrol of LC alignment is regarded as a unique optical hybrid system resulting from the appropriate combination of LCs as large birefringent media with photoresponsive surfaces.

Polymer-dispersed LCs (PDLCs)[11-13] and polymer-stabilized LCs (PSLCs)[14-18] are hybrid systems comprised of LC and polymer networks[19] exhibiting electrically driven light scattering or reflection and applicable to LC display devices[20] and holographic materials.[21,22] On the other hand, we have demonstrated recently that LC alignment is controllable by linearly polarized light irradiation of a novel hybrid system comprised of a low-mass LC and a crosslinked polymer network with azobenzene side chains.[23] The matrix-mediated photocontrol of LC alignment is achieved as a result of the marked amplification of azobenzene residues studded to polymer networks. One of the practical significances exists in the fact that this sort of volume-type cells possesses good transparency to visible light because of low loading of azobenzene residues. The efficiency and characteristics of LC photoalignment of this system may greatly depend on structures of azobenzene side chains because molecular interactions between LC and azobenzene residues play a critical role in thermal and optical properties. This situation led us to investigate the effects of *para*-substituents and spacer length of azobenzene side chains on photoinduced birefringence. We report here that the matrix-assisted LC alignment is controlled by linearly polarized light irradiation of a hybrid system comprised of LC and polymer network with various azobenzene derivatives. Furthermore, we demonstrate that the slantwise irradiation with non-polarized light of this composite system provides the novel way to achieve the three-dimensional control of the orientation of LC molecules.

EXPERIMENTAL

Chemical structures of materials used here are shown in Figure 1. A cell filled with LC / photoresponsive polymer network was fabricated according to our previous report.[11] A homogeneous solution of benzoyl

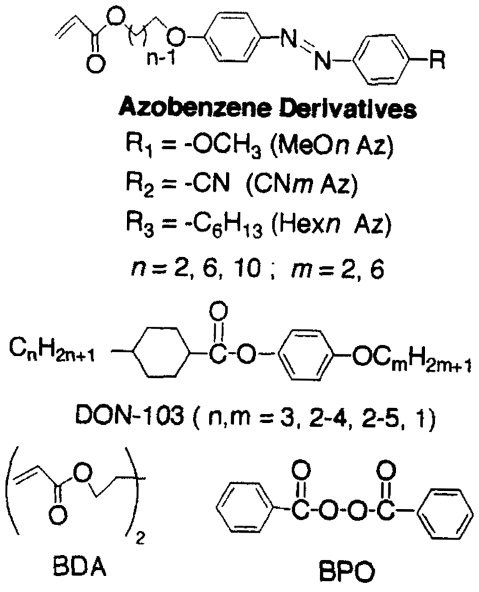


FIGURE 1 Chemical structures of compounds used in this study.

peroxide (BPO), an azobenzene derivative and a nematic LC, DON-103 (T_{NI} = 73 °C), in dichloromethane was evaporated *in vacuo* at room temperature, followed by mixing with 1,4-butanediol diacrylate (BDA). Hex*n*Az, MeO*n*Az and CN*m*Az denote azobenzene side chains substituted with hexyl, methoxy and cyano groups at the *para*-position group tethered to polyacylate backbones through spacer lengths (*n* and *m*) of *n* = 2, 6 and 10 and of *m* = 2 and 6, respectively. A mixture consisting of 5 wt% of BPO, 30 wt% of BDA, 3 – 5 wt% of an azobenzene derivative and 60 – 62 wt% of DON-103 was sandwiched between two cleaned glass plates and sealed. The cell gap was adjusted to be 25 μm by using film spacers. Orthoscopic observation was revealed that the mixture was in an isotropic phase. The cell was heated at 80 °C for 10 min to achieve the radical polymerization.

The polymerized cell was exposed to linearly polarized light or non-polarized light at 436 nm passing through suitable glass filters and a polarizer. A light source used was an ultrahigh-pressure mercury lamp (USHIO UI-501C) or a mercury-xenon lamp (SUPERCURE-202S, San-ei Electric MFG. Co.). The cell was heated on a hot stage during photoirradiation. Birefringence was calculated by retardation measurements of the cell, which were probed by a linearly polarized He-Ne laser beam. The direction of LC alignment was checked by conoscopic images and the crystal rotation method (BFA-150, JASCO Co.).

RESULTS AND DISCUSSION

Photocontrol of LC Alignment by Irradiation with Linearly Polarized Light

The polymerized cell showed weak light scattering at room temperature, indicating the occurrence of phase separation as a result of the polymerization. A clearing point as a transition temperature between nematic and isotropic phase (T_{NI}) was checked by orthoscopic observation and determined to be in the range of 47.5 – 59.0 °C for cells incorporating *p*-substituted azobenzene derivatives. The T_{NI} was much lower than that of pure DON-103, reflecting the contamination with various components.

Retardation measurements of cells were performed by passing a linearly polarized He-Ne laser beam through a cell and a crossed polarizer to monitor transmitted light intensity as a function of the rotational angle of a cell. Under these measurement conditions without propagation loss, the transmitted light intensity is expressed according to the equation (1):

$$T = \sin^2 (2\Phi) \sin^2 (k_0 \Delta n d/2), \qquad (1)$$

where Φ is an rotation angle of the cell, while k_0, Δn and d are the wavenumber in vacuum, birefringence and a cell gap (= 25 μm). To exclude experimental errors arising from light scattering, the following relation was used to obtain values of T:

$$T = I_{\mathrm{cross}} / (I_{\mathrm{cross}} + I_{\mathrm{para}}), \qquad (2)$$

where I_{cross} and I_{para} are the transmitted light intensity when the polarizer angle is set to be perpendicular to and in parallel with the electric vector of He-Ne laser light.

It was found that the photogeneration of birefringence depends on the structure of the azobenzenes. Figure 2 shows the birefringence as a function of temperature at which linearly polarized light irradiation of cells was carried out until the generation birefringence leveled off. Cells comprised of hexyl or methoxy substituted azobenzene derivatives shows

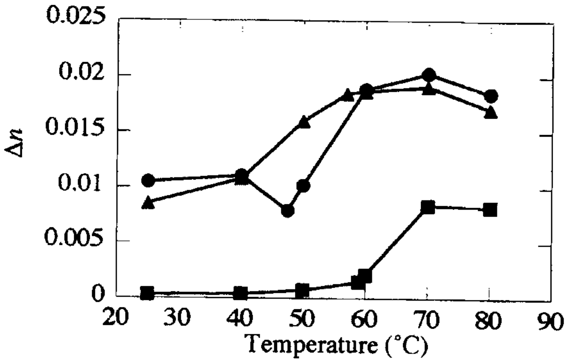


FIGURE 2 Photogenerated birefringence of cells fabricated with Hex2Az (filled circles), MeO2Az (filled triangles) and CN2Az (filled squares) as a function of cell temperatures after irradiation with linearly polarized 436 nm light of a 2.0 J cm^{-2} dose.

significant birefringence even though photoirradiation was achieved at room temperature (25 °C), while those comprised of the *p*-cyano azobenzene derivative exhibited only much small birefringence. The photobirefringence increases dramatically above T_{NI} for all cells. The cells fabricated with the *p*-hexyl or *p*-methoxy azobenzene displayed large birefringence of ca. 0.020 when the photoirradiation was made at 70 °C, while cells fabricated with the *p*-cyanoazobenzene showed small one of 0.008 when the cells were exposed to the light under the same condition. This suggests that the increase of the birefringence above T_{NI} is related to the phase change of the composite, leading to the decrease in viscosity of the LC and the increment of the mobility of polymer networks by heating to give rise to a suitable anchoring for LC alignment. The *p*-cyanoazobenzene has a large dipole moment so that molecular interactions between the *p*-cyanoazobenzene and less polar LC molecules are unsuitable to generate the photoinduced birefringence.

Figure 3 shows the photogenerated birefringence as a function of temperature when cells employing polymer networks substituted with *p*-methoxyazobenzene side chains through various alkylene spacer lengths

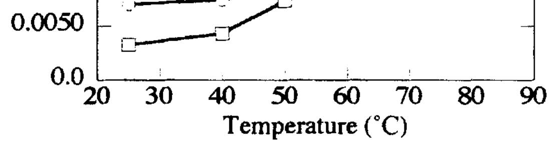
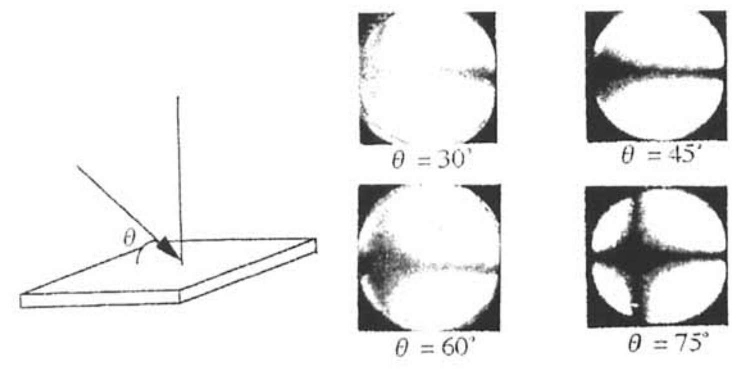


FIGURE 3 Photogenerated birefringence of cells fabricated with MeO2Az (filled circles), MeO6Az (open circles) and MeO10Az (open squares) as a function of cell temperatures after irradiation with linearly polarized 436 nm light of a 2.0 J cm^{-2} dose.

were irradiated with linearly polarized light until the photobirefringence was leveled off. A shorter spacer length resulted in larger photobirefringence. Cells fabricated with the *p*-cyano or hexylazobenzene also showed similar tendency of the photogenerated birefringence with respect to the alkylene spacer length. It is assumed that the alkylene spacer length plays no significant role to enhance molecular interactions between azobenzene moieties and LC molecules. Accordingly, we speculate that polymer networks restrict the flexibility of alkylene spacers.

Three-dimensional Orientational Control of Liquid-Crystalline Molecules by Slantwise Irradiation with Non-polarized Light

We have demonstrated that three-dimensional orientational control of LC molecules in volume-type cells comprised of LC and a crosslinked polymer networks with *p*-hexylazobenzene side chains is performed by slantwise irradiation with non-polarized light at 436 nm.[24] 4-Hexyl-4'-(2-acryloxyethoxy)azobenzene (Hex2Az) as a photoresponsive monomer to construct polymer networks was selected on account of its good generation of photobirefringence as described above. Figure 4 shows conoscopic images of a cell which was irradiated with slantwise non-



$\theta = 30°$ $\theta = 45°$

$\theta = 60°$ $\theta = 75°$

FIGURE 4 Conospopic images of a cell fabricated with Hex2Az after irradiation with non-polarized 436 nm light of a 1.0 J cm^{-2} exposure dose at various incident angles.

polarized light at various incident angles at 50 °C. The crosspoint of the images moves in consistence with changes in the incident angle of the light. The tilted orientation of LC was confirmed by the crystal rotation method. The present observation can be interpreted in a manner similar to our previous reports.[8,24] Irradiation with 436 nm light induces the repetition of *E* / *Z* photoisomerization of the azobenzene side chains to result in the molecular reorientation toward to the orientational direction of the molecular axis in parallel with the propagation direction of the light to minimize light absorption. Anisotropic orientation of LC molecules arises from side-by-side interactions of the reoriented azobenzene side chains with LC molecules to give anisotropic alignment. The anisotropic LC alignment was stable to prolonged slantwise irradiation with non-polarized light. Figure 5 shows the retardation obtained by the crystal rotation method when the cell was subjected to prolonged irradiation with non-polarized light. The shape of plots of the retardation does not change significantly at exposure doses of more than 30 J cm^{-2}.

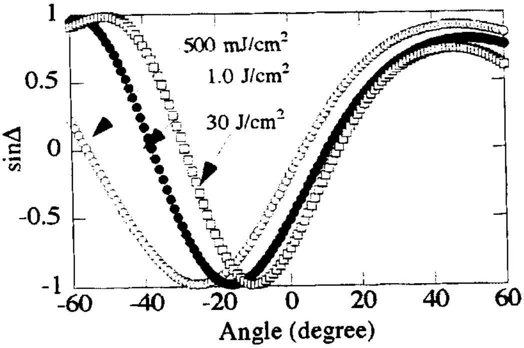


FIGURE 5 Retardation of a cell fabricated with Hex2Az after prolonged irradiation with non-polarized 436 nm light at an incident angle of 45° at 50 °C.

Photopatterning by Tilting Alignment of Liquid-Crystalline Molecules

The LC alignment by slantwise photoirradiation was used to make photopatterns in a volume-type cell as follows. A cell filled with the LC and crosslinked polymer networks was exposed to non-polarized 436 nm light of a 1.0 J cm^{-2} exposure dose at an incident angle of 30° on a hot plate heated at 50 °C. Subsequently, the photoirradiation under the same conditions was achieved through a photomask after changing an incident plane angle of the light by 90 °. Figure 6 shows one of the presentative patterns recorded by this technique. The photoimages observed by an

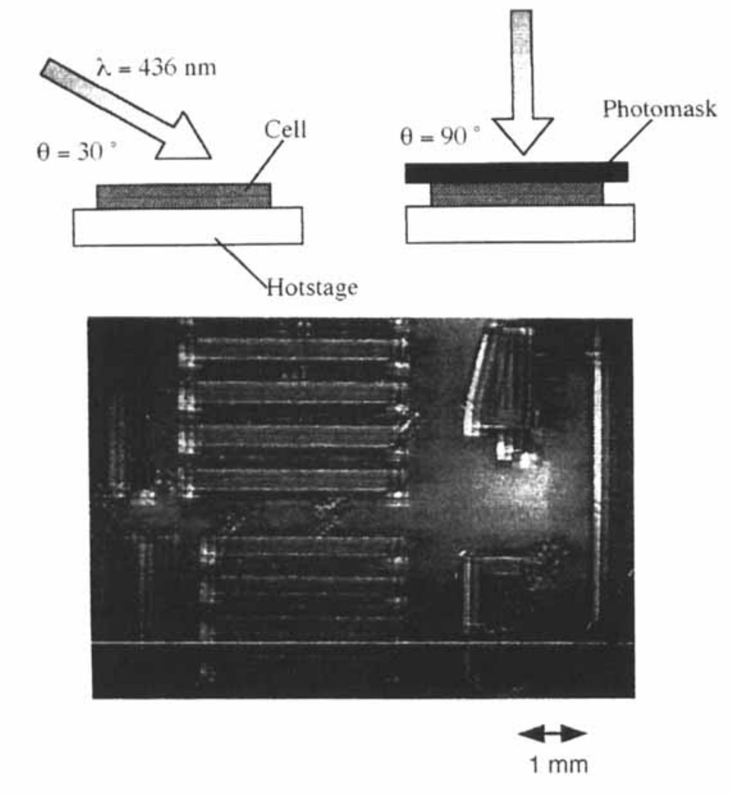


FIGURE 6 Polarized micrograph of a cell subjected to imagewise exposure to 436 nm light.

orthoscope arise from the difference in orientational directions of LC molecules determined by light propagation. The photogenerated LC alignment enhances the birefringence markedly so that the cell shows an excellent optical contrast. The photoimages were thermally stable and kept without any deterioration for prolonged storage at room temperature for more than a month.

CONCLUSIONS

Novel photoresponsive LC / polymer composites have been developed. Thermally stable birefringence is generated by the irradiation of cells filled with a nematic LC incorporated into crosslinked polymer matrix bearing azobenzene residues with linearly polarized 436 nm light. The photogeneration of birefringence is affected by the structure of azobenzene residues including *para*-substituent and alkylene spacer length. The photocontrol of three-dimensional orientation of LC molecules in this system has been realized by slantwise irradiation with non-polarized light. The direction of LC alignment corresponds to the incident angle of light and is rewritable by subsequent irradiation. Patterning is achievable by slantwise irradiation of non-polarized light through a photomask. The volume-type cells comprised of LC and polymer networks are applicable to novel photonic elements and devices.

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