Cooperative Reorientation of Dichroic Dyes Dispersed in Photo-cross-linkable Polymer Liquid Crystal and Application to Linear Polarizer

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The irradiation with linearly polarized ultraviolet light and subsequent annealing generated a large cooperative reorientation of a photo-cross-linkable polymer liquid crystal (PLC) film doped with a dichroic dye. The resultant film exhibited polarization efficiency of 98.1% and can be applicable to a linear polarizer. The fabrication of a patterned polarizer is also demonstrated using a photomask.

Polarizers are widely used for many kinds of optical devices to utilize the polarized light. A conventional linear polarizer is fabricated by mechanically drawing a polymer film, such as poly(vinyl alcohol) (PVA), doped with iodine or dichroic dye materials. The uniaxially oriented iodine complex or dichroic dyes along the stretched polymer backbone selectively absorb the incident light with parallel polarization. For the mechanically drawing method, a relaxation of the stretched film occurs at elevated temperatures and the fabrication of a patterned polarized element is impossible. Ichimura et al. reported the orientation of dichroic lyotropic liquid crystals (LCs) on a photoalignment layer of azobenzene-containing photoreactive polymeric films, based on the command surface technique using a linearly polarized (LP) light.[1–4] The influence of the surfactant/chromonic dye ratio on the orientation behavior of the dye was investigated in detail.[3] Optiva Inc. developed a thin film polarizer composed of lyotropic LCs directly coated on a substrate, which exhibited less off-axis light leakage than traditional polarizers.[5] Since the irradiation with a LP light controls the orientation direction of the photoalignment materials, micro-patterned polarizers can be realized by adjusting the polarization of the light exposure.[4]

Photoinduced reorientation of PLC to align LC groups besides the command surface technique was investigated using PLCs comprising photoreactive mesogenic groups.[6,7] We reported that a large in-plane reorientation of mesogenic groups was generated in a thin film of a photo-cross-linkable polymethacrylate LC with 4-(4-methoxycinnamoyloxy)biphenyl (MCB) side groups (PMCB6M: inset of Figure 1) by irradiating with an LP ultraviolet (LPUV) light and subsequent annealing in the LC temperature range of the polymer.[7] The adjusting the exposure doses can control the molecular reorientation direction both perpendicular and parallel to the polarization (**E**) of LPUV light.[7] If the reorientation of the mesogenic groups follows cooperative reorientation of dichroic dyes dispersed in the PLC film, linear polarizers and patterned polarization elements can be fabricated by the photo-process. This letter describes the fabrication of a linear polarizer film consisting of PMCB6M and a dichroic dye based on the photoinduced cooperative reorientation using a LPUV light. The influences of a composition of the dye and exposure doses on a cooperative reorientation behavior were investigated and a patterned polarizer film was demonstrated.

A thin film of PMCB6M dispersed with a dichroic azo-dye of N256, which was purchased from Hayashibara Biochem. Labs. Inc., and its chemical structure is not opened, was prepared by a spin-coating method on a quartz substrate from a chloroform solution. The N256 composition in PMCB6M was 10–40 wt %. Adjusting the PMCB6M/N256 concentration controlled the film thickness. A LPUV light exposure was performed using a high-pressure Hg lamp with a cut-off filter under 300 nm and Glan–Taylor polarizing prisms. The intensity was 150 mWcm^{-2} at 365 nm. The degree of the photoreaction was evaluated by monitoring the absorption spectroscopy. After irradiating, films were annealed at 150 °C for 4 min.

Figure 1 shows polarization absorption spectra of a PMCB6M/N256 (80/20 wt/wt) film before exposing, after exposing to the LPUV light and following subsequent annealing. The degree of the photoreaction, which included both [2+2] cycloaddition reaction and photoisomerization of the cinnamoyl groups, was approximately 15 mol %. After exposure, a small optical anisotropy around 310 nm appeared, while absorption bands of N256 around 580 nm did not change, indicating that the exposing to LPUV light only causes the axis-selective photoreaction of the mesogenic groups of PMCB6M. Annealing procedure generated great amplification of the optical anisotropy of both PMCB6M and N256 parallel to **E**. This means that the thermally enhanced reversion of the photoinduced optical anisotropy of PMCB6M follows a cooperative reorientation of N256 parallel to **E**. The thermally generated in-plane order parameter, *S* $(= (A_{\parallel} - A_{\perp})/(A_{(\mathrm{large})} + 2A_{(\mathrm{small})}))$, where $A_{\parallel}$ and $A_{\perp}$ are the ab-

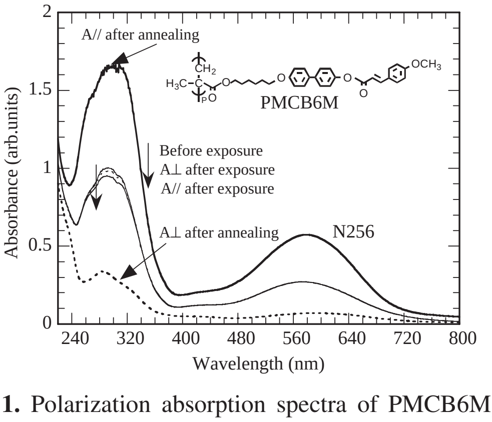

Figure 1. Polarization absorption spectra of PMCB6M/N256 (80/20 wt/wt) film before exposing, after exposing to LPUV light and following subsequent annealing. Thickness: 300 nm. Solid and dotted lines exhibit the spectrum parallel ($A\|$) and perpendicular ($A\perp$) to the polarization of LPUV light, respectively.

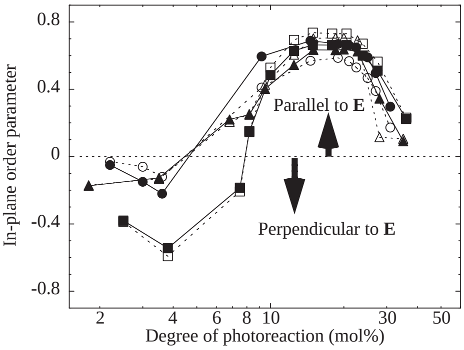

Figure 2. Thermally enhanced in-plane order parameter of MCB at 315 nm (closed points) and N256 at 584 nm (open points) as a function of degree of photoreaction. N256 content: 10 wt % (circles), 20 wt % (triangles), and 30 wt % (squares).

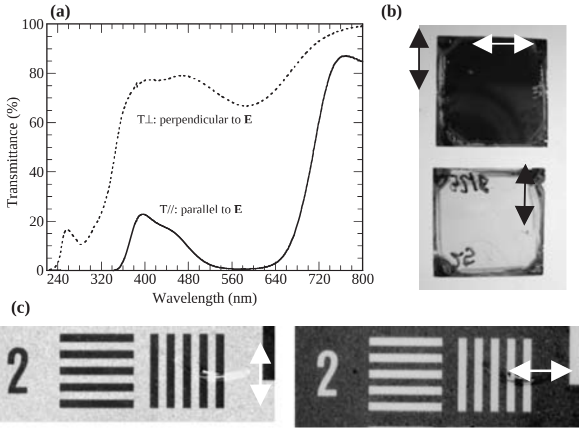

Figure 3. (a) Polarized transmission spectra and (b) photographs of reoriented PMCB6M/N256 (70/20 wt/wt) films on a linear polarizer. Arrows indicate the reorientation and polarization direction. (c) A patterned PMCB6M/N256 (70/30 wt/wt) film on a linear polarizer. Line/space is 22/22 μm/μm. Degree of the photoreaction was 5 and 17 mol %, respectively.

sorbances parallel and perpendicular to polarization of LPUV light **E**, respectively, and $A_{(\mathrm{large})}$ is the larger of $A_{\parallel}$ and $A_{\perp}$, and $A_{(\mathrm{small})}$ is the smaller), at 315 and 584 nm are 0.64 and 0.71, respectively. The *S* value of PMCB6M is similar to a film without N256,[7] indicating that the reorientation of MCB groups is not restricted by the cooperative reorientation of N256.

The influences of the concentration of N256 and exposure doses on the cooperative reorientation of PMCB6M/N256 films were evaluated. Figure 2 plots thermally enhanced *S* values of PMCB6M/N256 film (thickness = 200 nm) as a function of degree of the photoreaction. When the N256 concentration was greater than 40 wt %, crystallization of N256 occurred after annealing the exposed film. When the N256 concentration was 30 wt %, both N256 and MCB groups reoriented perpendicular to **E** at the early stage of the photoreaction. Cooperative reorientation perpendicular to **E** was small for the 10 and 20 wt % of N256 concentration. In contrast, large in-plane order parallel to **E** was obtained when the degree of the photoreaction was approximately 12–20 mol %. These results indicate that N256 cooperatively reorients along the reorientation direction of the MCB groups.[7]

To fabricate a linear polarizer, cooperative reorientation of a thick film was investigated. Figures 3a and 3b show transmission spectra of an oriented 600-nm-thick PMCB6M/N256 (80/20 wt/wt) film and its photograph when the degree of the photoreaction is 15 mol %. The orientational order of N256 was 0.82. This value is larger than that of a thin film (Figure 2). The larger *S* values for thick films were observed when the N256 concentration was 10 and 30 wt %. A further investigation of an influence of the film thickness on the reorientation of N256 is in progress. The polarizing efficiency, PE $(= (T_{\perp} - T_{\parallel})/(T_{\perp} + T_{\parallel})$, where T means the transmittance of the film), of the reoriented film at 584 nm of the film is 98.1%, indicating that this film can be used as a linear polarizer. However, since the film only contains N256 as the dichroic dye, other dichroic dyes should be dispersed to cover the whole visible region.

Finally, a patterned linear polarizer was fabricated using a photomask by adjusting the exposure doses without changing the polarization of LPUV light. Figure 3c shows an orthogonally-patterned linear polarizer fabricated using a photomask. Since the adjusting the exposure doses controlled the cooperative reorientation direction, polarization direction of the transmitted light can be regulated according to the photomask-pattern.

In summary, the cooperative reorientation of photoreactive PMCB6M film dispersed with a dichroic dye of N256 induced by irradiating with LPUV light and subsequent annealing was demonstrated. The dichroic dye was reoriented parallel to the reorientation direction of PMCB6M when the content of the dye was up to 30 wt %. The in-plane reorientation order parameters of both materials are greater than 0.7 and the resultant film act as a linear polarizer. By using a photomask, a patterned polarizer was fabricated with orthogonal polarization direction, which will be useful for a binocular disparity stereoscopic display. Further study on the cooperated reorientation behavior of other types of dichroic dyes is underway.

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