Circular Arrangement of Mesogens Induced in Bragg-type Polarization Holograms of Thick Azobenzene Copolymer Films with a Tolane Moiety

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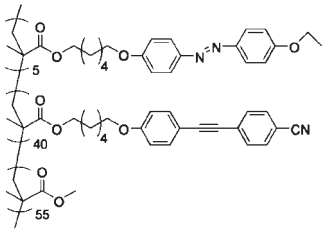
Bragg-type polarization holograms were recorded in thick copolymer films with tolane and azobenzene moieties by interfering two orthogonal circularly polarized beams at 488 nm. Observation of the films with a polarizing optical microscope revealed that circular alignment of molecules was induced along a grating vector. An incident reading beam at 633 nm was efficiently diffracted, depending on its polarization state and incident direction.

Since hologram is one of promising media to record and read out a large amount of data, holographic data storage systems have been intensively studied from the viewpoint of high-storage capacity, short access time, and high data-transfer rate.[1,2] In holographic materials, many aspects such as high diffraction efficiency, fast response, high resolution, high sensitivity, temporal stability, and rewritability must be considered. Even though a number of holographic materials have been proposed up to now, azobenzene polymers seem to be one of the most suitable rewritable holographic materials because of their high sensitivity and reversibility.[2–9] Azobenzene, which undergoes reversible changes in conformation between trans and cis isomers, is one of the most popular photochromic materials. Moreover, upon exposure to linearly polarized light, trans-azobenzene molecules become aligned perpendicular to an electric field of light through repetition of trans–cis–trans isomerization cycles. We have reported that a large change in refractive index can be brought about in a series of azobenzene liquid-crystalline polymers, and applied to high-performance holograms.[8] Recently, it has been revealed that thick azobenzene copolymer films with a mesogenic moiety give rise to ≈100% diffraction efficiency in the Bragg regime and high multiplicity of 55.[9] In particular, a fast increase of diffraction efficiency was observed when polarization holograms were formed with two orthogonal circularly polarized beams. However, their molecular arrangement and diffraction properties have not been investigated in detail. Here, we report circular arrangement of mesogens in polarization holograms recorded with orthogonal circularly polarized beams and their distinct polarization dependence of an incident reading beam on diffraction efficiency.

Figure 1 shows the structure of the copolymer with azobenzene and tolane moieties used in this study. Detailed procedure in preparation of the polymer was reported previously.[9] Molecular weights and thermodynamic property are also shown in Figure 1. Thick polymer films were prepared by hot pressing the copolymers with a pair of glass plates, with silica spacers with thickness of 100 μm between them, on a hot stage at 180 °C for 30 min, and then by annealing at 150 °C for 2 h. The film thickness was confirmed by UV–vis spectroscopy.



M_n = 30,000; M_w/M_n = 1.9; G 61 I

Figure 1. Chemical structure, molecular weights, and thermodynamic property of the polymer used in this paper. M_n, number-average molecular weight; M_w, weight-average molecular weight; G, glassy; I, isotropic.

Orthogonal circularly polarized beams at 488 nm from an Ar^+ laser were employed as writing beams. Two beams were interfered on the film at an incident angle of 7° (Figure 2a). The total intensity of the writing beams was adjusted at 200 mW/cm^2. The formation of gratings was evaluated by monitoring the first-order diffraction beam at 633 nm from a He–Ne laser with a photodiode in real time. The reading beam was incident to the film at angles of +9.3 or −9.3°. All the experiments were carried out at room temperature. Diffraction efficiency (η) was defined as the ratio of the intensity of the first-order diffraction beam (I_1) to that of the transmitted beam (I_0) through the sample film as expressed by the following equation:

$$\eta(\%) = \frac{I_1}{I_0} \times 100. \quad (1)$$

Upon exposure to the writing beams, only a single diffraction beam was observed, which is attributed to the formation of gratings in the Bragg regime. Gratings formed with orthogonal circularly polarized beams, were observed with a polarizing optical microscope (Olympus BX-50, BH-2), and their textures are shown in Figures 2b and 2c. Periodic bright fringes were formed along the grating vector (Figure 2c, $\theta = 0°$). This indicates that the periodic alignment of both azobenzene and tolane moieties is successfully induced,[10] resulting in the periodic change in refractive index. To investigate the optical anisotropy caused by the molecular alignment, we observed the gratings by rotating the polarizer and analyzer simultaneously by every 30°, maintaining the grating vector at $\theta = 0°$. It was revealed that the bright fringes shifted along the grating vector by the rotation of the polarizer and analyzer, and the initial pattern recovered at $\theta = 180°$. Interference of two orthogonal circularly polarized beams produces periodic modulation of polarization direction of linearly polarized light. Irradiation with a linearly polarized beam brings about trans–cis–trans photoisomerization of the azobenzene moiety, leading to perpendicular alignment of the azobenzene (Figure 2d). Bright fringes are observed only at

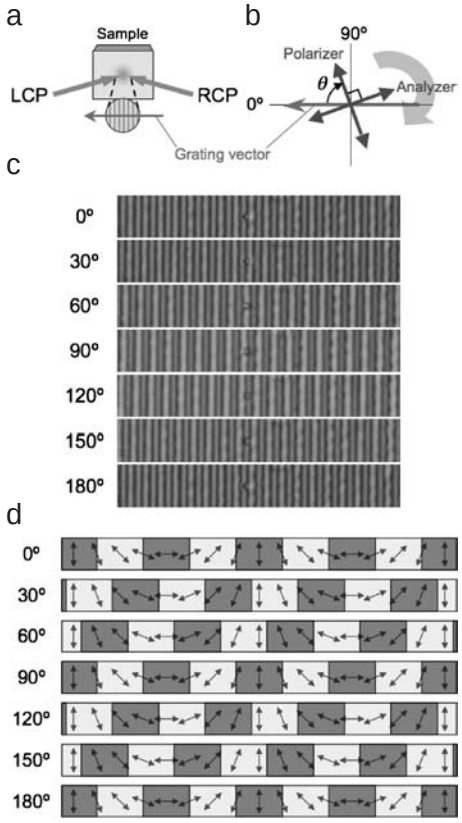


Figure 2. Observation of the holograms by polarizing optical microscopy. (a) Optical setup for formation of holograms with left circularly polarized (LCP) and right circularly polarized (RCP) beams. (b) Arrangement of the grating vector and the polarizer. (c) Polarizing micrographs observed as a function of the rotation angle of the polarizer and analyzer, θ. (d) Alignment of mesogens induced in holograms. Arrows indicate the direction of mesogens. White and gray areas correspond to bright and dark areas in (c), respectively.

the areas where the molecules are aligned neither parallel nor perpendicular to the polarizer under observation by polarizing optical microscopy. Therefore, the shift of the fringes clearly indicates that the circular arrangement of mesogens is induced as shown in Figure 2d.

We investigated the effect of the polarization state of the reading beam on diffraction efficiency by rotating a quarter-wave plate (Figure 3a). The diffraction efficiency strongly depended on the polarization state. High diffraction efficiency of 80% was obtained with a right circularly polarized (RCP) beam, while no diffraction was observed with a left circularly polarized (LCP) beam when the reading beam was incident from the right (R) side (Figures 3b and 3c). On the other hand, when the reading beam was incident from the left (L) side, only the LCP beam was efficiently diffracted. The distinct polarization dependence supports that circular arrangement of mesogens suggested in Figure 2d is induced in the film. To the best of our knowledge, this is the first example of holograms showing polarization sensitivity and incident angle selectivity of the reading beam simultaneously. We believe that such polarization-sensitive Bragg holograms can play an important role in fabrication of novel optical devices.

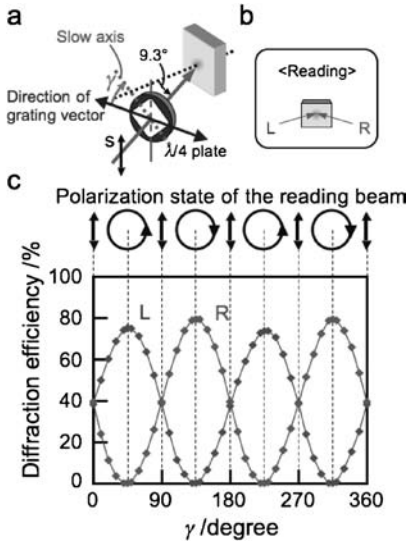


Figure 3. Effect of polarization state of the reading beam on diffraction efficiency. (a) Arrangement of a quarter-wave plate: the probe beam was incident from the right (R) side. (b) Incidence of the probe beam from the right (R) and left (L) sides, which correspond to the incident angles of 9.3 and -9.3°, respectively. (c) Diffraction efficiency as a function of the polarization state.

References and Notes

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10 The diffraction efficiency strongly depended on the tolane contents (ref. 9), which means that the change in alignment of the tolane moiety is cooperatively induced by the azobenzene moiety.

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