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Polarization holographic gratings in an azobenzene copolymer with linear and circular photoinduced birefringence

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ABSTRACT

Polarization holographic recordings in an azobenzene copolymer were performed by using the interference of two linearly orthogonally polarized beams. The first order diffraction efficiency of the recorded gratings was modulated by the polarization direction of the probe beam as a consequence of the spatial modulation of the linear and circular photoinduced birefringence. The polarization of the diffractive wave was also strongly dependent on the polarization of the readout wave. The value of the photoinduced linear and circular birefringence was evaluated through Jones matrix calculations, and the obtained values were experimentally confirmed to be valid by single beam excitation measurements.

1. Introduction

Creating anisotropic structures in azobenzene-containing polymeric films by means of irradiation has received a lot of attention because of possible applications in optical data storage [1,2], polarization holograms[3], and optical devices [4,5]. Most of the studies in the literature focused on the photoinduced linear anisotropy which is based on the axis-selective trans–cis–trans isomerization and reorientation of azobenzene groups since irradiating with linear polarized light [6–9]. In addition to the photoinduced linear anisotropy, chiral structures, whose handedness depends on the helicity of the light, were also optically induced in some azobenzene polymer films after irradiation with a circularly or elliptically polarized light. This phenomenon, known as chiroptical switching, becomes one of the principal and intriguing functionalities in azobenzene molecular systems [10–15]. The created chiral features can strongly affect the polarization state of the light propagating through the sample [16,17]. Since the polarization properties of the holographic gratings are strongly dependent on the photoinduced anisotropic structures induced during the recording processes, the appearance of the circular anisotropy is very important in practical use of polarization gratings, providing several advantages for creation of a new generation of materials with increasing functionalities [18–21].

Although many studies have been performed to investigate the polarization holography recording in azo materials, the photoinduced orientation of azo groups was generally limited to the poor solubility and stability of molecules and needs quite long time to achieve uniform alignment [22,23]. In the present paper, we have investigated the holographic recording in an azobenzene copolymer which is capable of undergoing light-induced generation of large linear and circular anisotropy. This copolymer possesses good optical performance and stabilities due to the molecular cooperative motion between two azobenzene chromophores. Additionally, an increase flexible spacer of the photochromic units can also enhance the inscription process. We demonstrate the effective polarization modulation induced by linear and circular birefringence in the recorded polarization gratings. According to the experimental phenomena and some calculations based on the Jones analysis, the amplitude of the linear and circular birefringence was obtained.

2. Experimental details

The copolymer containing azobenzene and azopyridine in side-chain was synthesized as follows: 4 mmol azobenzene monomer, 1 mmol azopyridine monomer and 5% AIBN (azoisobutyronitrile) were dissolved in 15 ml tetrahydrofuran (THF). The reaction mixture was bubbled with argon for 30 min and the mixture was heated to reflux for 24 h under argon. Finally, the reaction mixture was cooled down to room temperature and it was added dropwise into a large amount of methanol (400 ml). The precipitate was filtered and the obtained solid was redissolved into THF and precipitated into methanol again. The obtained solid was then dried

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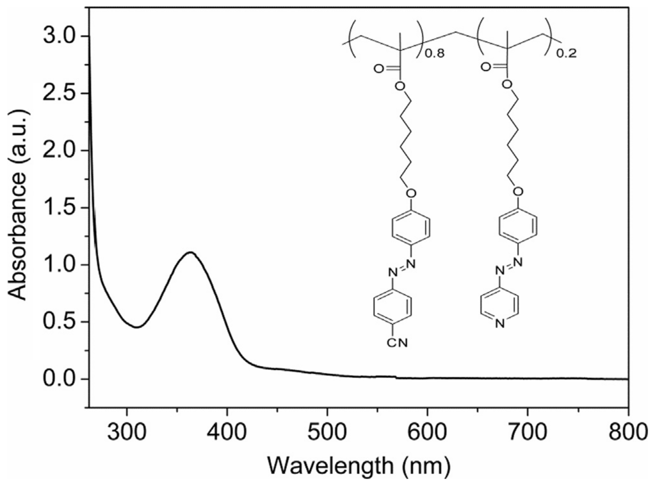

Fig. 1. UV–vis linear absorption spectrum of the polymer film. The inset is the molecular structure of the polymer.

under vacuum at ambient temperature for 72 h to provide the desired product. Its molecule structure is shown in the inset of Fig. 1. The film of about 1 μm was obtained by casting the $CHCl_3$ solution of polymer on to clean glass substrates and drying it for 24 h at 40 °C vacuum incubator. Fig. 1 shows the UV–vis linear absorption spectrum of the polymer film.

Polarization holographic gratings were recorded by two 488 nm beams from an Ar^+ laser with the intensity of 100 mW/cm^2. The experimental arrangement was presented in our previous work [3]. The polarization of the recording beams was controlled by half-wave plate and the crossing angle between the two writing beams was 15°, resulting in a spatial periodicity of 1.9 μm. Two polarized configurations were performed by the interference of two linearly orthogonally polarized beams, and their polarizations were set to be at ±45° to the horizontal in one case and at 0 ° and 90° in the other case. A low-power continuous diode laser light at 650 nm was used to read out the ±first-order diffraction signal. The recording time in all the experiments is about 1 min. The analysis of their diffraction properties was performed after the recording process. A rotating analyzer placed on the transmitted probe beams path, between the sample and a photodetector, has been used to characterize the polarization state of the ±first-order diffracted beams.

The photoinduced birefringence was investigated with a continuous diode laser at 650 nm as the probe light, which is far from the absorption band of the photochromic azo groups, and an Ar^+ laser at 488 nm as the pump light. For the measurement of photoinduced linear photobirefringence, the sample was placed between two crossed polarizers in the path of the probe light, and the pumping beam was linearly polarized at ±45° with respect to the direction of polarizers. All the signals were measured by the photo-diode and lock-in amplifier. The linear birefringence value were calculated by [1]

$$I_\perp = I_0 \sin^2(\pi \Delta n_{lin} d/\lambda), \quad (1)$$

where $I_\perp$ is the intensity of the probe beam passing through the crossed polarizers, I_0 is the probe intensity passing through the parallel polarizers before pump irradiation, λ is the probe wavelength and d is the film thickness.

For the measurement of photoinduced circular birefringence, the pump beam was set to be circularly polarized, and the polarization direction of the linearly polarized probe beam was set to be slanted 45°. The probe beam was passed through the sample, and the Glan–Thompson prisms were placed behind the sample. The laser-induced circular photobirefringence is obtained as [2,3]

$$\Delta\varphi_{cir} = \frac{2\pi d \Delta n_{cir}}{\lambda} = \tan^{-1}\left(\frac{S_1}{S_2}\right), \quad (2)$$

$$S_1 = I_0 - I_{90}, \quad (3)$$

$$S_2 = I_{45} - I_{135}, \quad (4)$$

where I_q represents the transmitted intensity when the angle between the optic axis of the Glan–Thompson prisms and horizontal axis in the fixed laboratory axes is q, which can be determined from experimental observation.

3. Results and discussion

It is known that the resultant light field of two coherent waves with mutually orthogonal polarizations has a constant intensity with a polarization state that is periodically modulated, as shown in Fig. 2. We consider the polarization interference pattern formed by the interaction of two plane waves $\vec{E_1}$ and $\vec{E_2}$, with equal amplitudes I. According to the Jones Matrix formalism, as reported in Refs. [17–20], the transmission matrixes for ±first-order diffracted terms can be simplified as

$$\overleftrightarrow{T}_{\pm1}^{\pm45} = \frac{i\exp(\pm i\delta)}{2}\begin{bmatrix} \Delta\varphi_{lin} & \mp\Delta\varphi_{cir} \\ \pm\Delta\varphi_{cir} & -\Delta\varphi_{lin} \end{bmatrix}, \quad (5)$$

when the polarization of the recording beam are at +45° and −45°, and

$$\overleftrightarrow{T}_{\pm1}^{0-90} = \frac{i\exp(\pm i\delta)}{2}\begin{bmatrix} 0 & \Delta\varphi_{lin} \mp \Delta\varphi_{cir} \\ \Delta\varphi_{lin} \pm \Delta\varphi_{cir} & 0 \end{bmatrix} \quad (6)$$

when the polarization of the recording beams are at 0 ° and 90°, respectively. Here, $\delta = 2\pi x/\Lambda$, $\Delta\varphi_{lin} = \pi\Delta n_{lin} d/\lambda$, $\Delta\varphi_{cir} = \pi\Delta n_{cir} d/\lambda$, where Δn_{lin} is the photoinduced linear birefringence, Δn_{cir} is the photoinduced circular birefringence, Λ is the grating spacing, d is the thickness of the polymer film and λ is the probe light beam wavelength.

In order to determine the diffraction efficiency and the polarization properties, we consider the diffracted light field $\vec{E}_{\pm1} = \vec{T}_{\pm1} \cdot \vec{R}$, where $\vec{R}$ is the light field of the probe beam, and give a discussion and some calculations. When the probe beam is linearly polarized, the electric field can be written as

$$\vec{R} = \begin{bmatrix} \cos\alpha \\ \sin\alpha \end{bmatrix}, \quad (7)$$

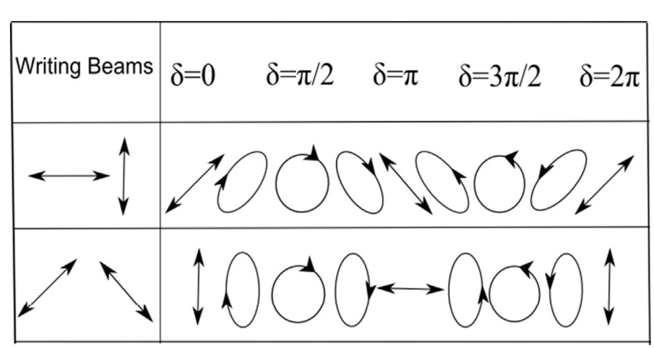

Fig. 2. The periodic polarization modulation of the interference light filed in recording with two waves with orthogonal linear polarizations.