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Photoinduced anisotropy in an azo-containing ionic liquid–crystalline polymer

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ABSTRACT

Photoinduced anisotropy in an azobenzene ionic liquid–crystalline polymer was investigated through dichroism, birefringence and polarization holography. A dichroism degree of 1.58 and a birefringence value $\Delta n \sim 10^{-2}$ were achieved in the polymer film at room temperature, and the polymer film was found to possess the characteristics of reversible and long-term optical storage. Particularly the stored birefringence could be enhanced to $\Delta n \sim 10^{-1}$ by annealing the film, and it is attributed to the thermal self-organization of the molecules. Furthermore, linear- and circular-polarization holographic recordings were accomplished in the polymer film and pure polarization gratings were produced.

1. Introduction

In the past decades, numerous studies of optical storage have been done to azobenzene containing polymers because of their good photoactive characteristics [1]. It is well known that azobenzene molecules can undergo *trans–cis–trans* isomerization cycles under the irradiation at a wavelength lying in the absorption region. If the pump light is linearly polarized, the molecules are oriented perpendicular to the pump polarization direction [2]. This photoinduced orientation results in macroscopic anisotropy, thus the dichroism and birefringence in polymer films. The dichroism represents the absorbance variations along the directions parallel and perpendicular to the pump polarization, while the birefringence represents the phase modulation effect of the photo-oriented polymer film. In particular, the real-time behavior of photoinduced birefringence has been widely investigated, because it can provide a direct insight into the orientation process expediently [3–5]. Based on the characterization of photoinduced anisotropy in azobenzene polymers, much attention has been paid to polarization holographic recordings, because pure polarization gratings are useful for highly functionalized optical devices that can control both the beam propagation direction and polarization state [6–8]. Polarization gratings are written by two waves with mutually orthogonal linear or circular polarization, in which the resulting light field is modulated by polarization only. Since azobenzene molecules can be oriented perpendicular to the pump polarization, irradiating with a light field whose polarization state is periodically modulated in space produces polarization gratings in the films. Compared to the gratings written by an intensity-modulated light field, the polarization gratings can also offer higher diffraction efficiency and signal-to-noise ratio [9,10], which is promising in the applications of optical storage.

On the other hand, high quality of the photoinduced anisotropy is crucial for the practical use of optical storage. The anisotropy behavior of azobenzene polymers depends mainly on the concentration of azobenzene molecules, the chemical structure, the pump intensity and the temperature [11,12]. Setting aside the external experimental conditions, one effective method of achieving high quality of the anisotropy is to use eligible materials. For this purpose, azobenzene liquid–crystalline polymers have been developed extensively for their large magnitude and superior stability of the photoinduced anisotropy [13–15]. In the present work, we employed a novel ionic liquid–crystalline polymer containing azobenzene groups, which was found to possess good stability of the anisotropy. The characteristics of photoinduced anisotropy were detailedly investigated through dichroism, birefringence and polarization holography. Impressively, the birefringence value could be largely amplified by a thermal treatment, and a brief discussion is presented. Furthermore, pure polarization gratings were

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written in the film by both linear- and circular- polarization holographic recordings, and their polarization properties were studied.

2. Experiment

2.1. Material and film preparation

The sample is a supramolecular material by the ionic self-assembly of poly(ionic liquid) (PIL) and azobenzene dye, the molecular structure of which is shown in Fig. 1a. The charged polymer Poly(1-butyl-vinylpyridinium bromide) (PIL) was selected as the main chain segment, and the methyl orange (MO) dye was selected as the building unit due to its capability for photo-isomerization. For the preparation of ionic self-assembly complex, 2 mg/ml PIL aqueous solution was added dropwise to MO aqueous solution with the same concentration, i.e. in a 1:1 molar charge ratio. The precipitated complex was filtrated and washed several times with doubly distilled water to remove residual salts and possible noncomplexed precursors, then dried in vacuum at 60 °C for 12 h. Polarized optical microscopy with hot stage was performed and displayed that the complexes powder melt at about 180 °C and the Schlieren textures appeared during cooling. The pronounced Schlieren textures indicated high orientational order of the complexes. In order to put more insight into the phase present in the material, small-angle X-ray diffraction measurement was performed to the complex. As shown in Fig. 1b, the annealed PILMO has a reflection peak q at $2\theta = 3.0°$ corresponding to a d-spacing of 2.9 nm, along with well defined $2q$ ($2\theta = 6.0°$) and $3q$ ($2\theta = 9.0°$), suggesting lamellar organization of smectic structure. The complex films were prepared by spin-coating a chloroform solution (30 mg/ml) onto the glass slides (speed: 2000 rpm, time: 18 s). The thickness of the resultant films was about 275 nm, measured by a Dektak profilometer. The absorption spectra of the complex films is shown in Fig. 2.

2.2. Experimental setup

For the measurements of photoinduced dichroism, an S polarized argon-ion 488 nm laser beam was employed as the pump light. The diameter of the beam was expanded to 15 mm by a lens, so the film could be fully irradiated. The average pump intensity over the illumination area was 60 mW/cm^2, and the exposure time was 20 min. After the pump irradiation, polarized spectra of the polymer film were measured with the help of a Glan–Taylor prism.

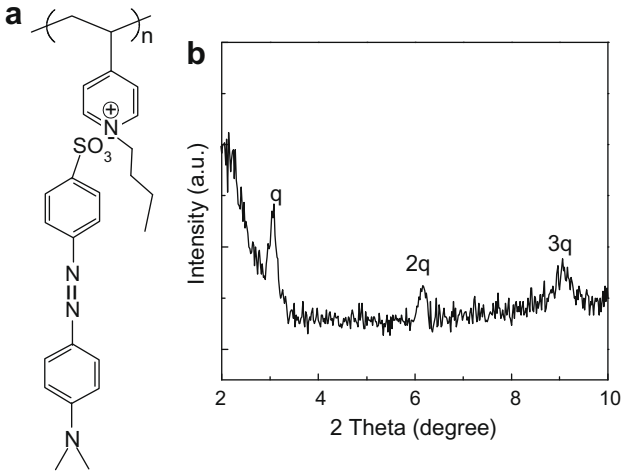

Fig. 1. (a) Molecular structure of the complex PILMO; (b) Small-angle X-ray diffraction diagram of the PILMO films annealed from isotropic phase.

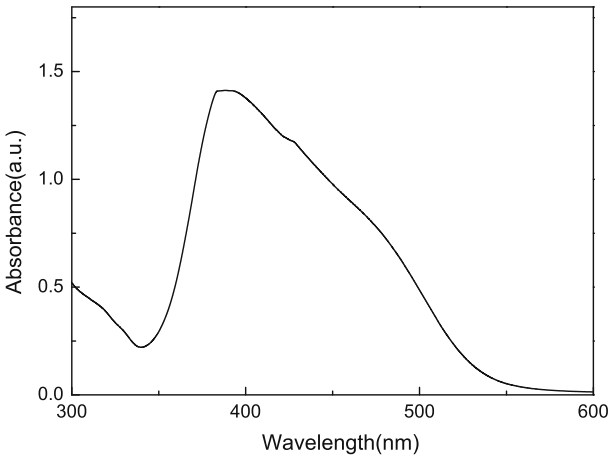

Fig. 2. Absorption spectra of the complex film of PILMO.

The prism was placed between the lamp and the film in spectrophotometer, thus the probing polarization direction can be controlled.

The experimental setup for photoinduced birefringence measurements is shown in Fig. 3a. A continuous 532 nm laser beam was employed as the pump light, and a 650 nm diode laser beam which is outside the absorption band of the sample was employed as the probe light. The polymer film was placed between two crossed polarizers in the path of the probe light, and the pump light was set to linearly polarized at ±45° with respect to the polarizers. The transmitted probe signal was measured by the photo-detector and lock-in amplifier. After the birefringence was photo-induced at room temperature, the thermal behavior of the stored birefringence was studied with a temperature controller.

Fig. 3b shows the experimental setup for polarization holographic recordings. The gratings were written by two 532 nm beams with equal intensities of 200 mW/cm^2, interfering on the film at an angle of 15°. Two polarization combinations (S–P and RCP–LCP) of the writing beams W_1 and W_2 were employed. Here S and P refer to a beam polarized perpendicular and parallel to the incidence plane, respectively; while RCP and LCP refer to right-hand-side and left-hand-side circularly polarized beams,

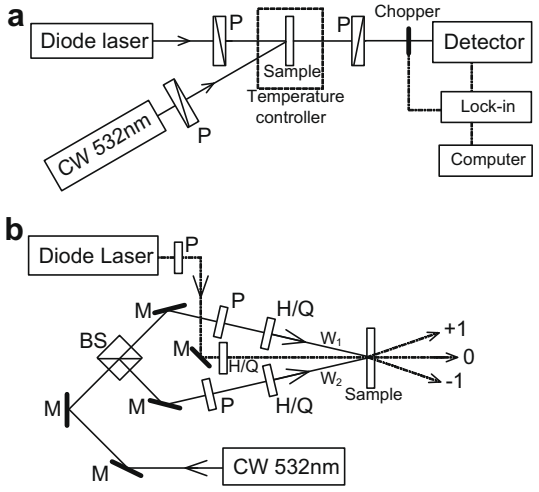

Fig. 3. Experimental setup for (a) photoinduced birefringence detection, and (b) polarization holographic recordings. P, polarizer; BS, beam splitter; M, mirrors; H and Q refer to the half-wave and quarter-wave plate, respectively.