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High diffraction efficiency polarization gratings recorded by biphotonic holography in an azobenzene liquid crystalline polyester

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High diffraction efficiencies have been achieved with polarization gratings recorded in thin films of an azobenzene side-chain liquid crystalline polyester by means of biphotonic processes. Efficiency values up to 30% have been reached after an induction period of 300 s and subsequent evolution with the sample in darkness. These values are at least two orders of magnitude higher than those previously reported for biphotonic recording. The gratings can be erased with unpolarized blue light and partial recovery of the diffraction efficiency has been observed after the erasure process when the sample is kept in darkness. Red light illumination of the erased film increases the recovered efficiency value and the recovery rate. © 2001 American Institute of Physics. [DOI: 10.1063/1.1379791]

Polymer films containing azobenzene units have been intensively studied because they are promising systems for optical applications such as holographic^{1–3} and digital storage,⁴ liquid crystal command surfaces,⁵ and nonlinear optical devices.⁶ Holographic recording performed with blue light from an Ar⁺ laser in this kind of material has been reported by several groups. High diffraction efficiencies (up to 80%)² have been obtained in gratings generated with a polarization modulated pattern.⁷ The appearance of periodic surface relief structures associated with the optical recording has also been observed in these films.^{8,9}

From a technological point of view it is of interest to shift the recording wavelength to the red region, where an inexpensive diode laser could be used. In order to achieve this goal in azobenzene compounds, two strategies have been followed. On the one hand, it is possible to redshift the absorption spectra by increasing the strength of the acceptor and donor substituents.^{10,11} In addition, holographic recording can also be performed with coherent red light using biphotonic processes.^{12,13} In these processes an incoherent blue light source is used to generate a *cis* population. Thus, the polymer film becomes sensitized to light in the red region and recording is performed with a coherent red light source.¹⁴

We have recently reported holographic recording in liquid crystalline side-chain polymers by means of biphotonic processes using a blue lamp and a He–Ne laser.^{15,16} Holographic gratings induced with red light intensity or polarization modulated patterns (henceforth referred to as intensity and polarization gratings, respectively) have been produced. However, one of the problems associated with biphotonic

holographic recording concerns the low values reached to date for the diffraction efficiencies (up to 0.02% in guest–host systems¹³ and 0.2% in liquid crystalline polyester films),¹⁵ which are far from the high values obtained in the same films by recording with coherent blue light. In an attempt to improve the diffraction efficiencies obtained with biphotonic processes we decided to study films consisting of the side-chain liquid crystalline polyester P6a4 (see Ref. 17). It has been reported that films of this polyester, when irradiated with light from an Ar⁺ laser and then exposed to the polarized light from a He–Ne laser, show an alignment of the azobenzene chromophores. The alignment is parallel to the polarization direction of the He–Ne with order parameters of up to 0.5 (see Ref. 18). This situation suggests the possibility of obtaining strong orientation effects and, consequently, high diffraction efficiencies with polarization gratings induced in P6a4 films using biphotonic holography.

The synthesis and characterization of P6a4 have been described previously.^{17,19} The T_g of the polymer is $\sim 10^\circ\text{C}$ and the material shows a bilayer smectic A mesophase between 45 and 59 °C. The polymer crystallizes only upon prolonged annealing at room temperature (RT) during several days due to the hindered kinetics of crystallization.¹⁹ Films were prepared by casting a solution of 2 mg of the polymer in 150 μl of chloroform on glass substrates. The film thickness was measured with a profilometer and values of about 1 μm were obtained. Prior to performing any experiment, films were heated up to 80 °C in order to erase any possible effects due to the morphology induced during film preparation. The films were then rapidly cooled down to RT by placing them on a cold metal plate. All the experiments were performed at RT.

The experimental setup used for polarization holography measurements is shown in Fig. 1. The red light from a

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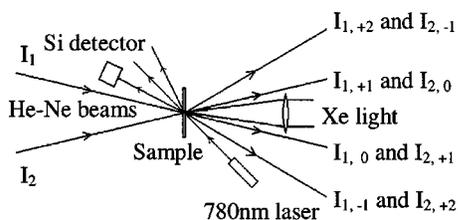


FIG. 1. Biphotonic polarization holographic setup showing the recording (I_1 and I_2) and diffracted beams ($I_{i,j}$) of the He-Ne laser.

He-Ne laser was split into two beams (I_1 and I_2), each of about 375 mW/cm^2 , and these beams were made to interfere on the film at an angle of 3.6° . The two recording beams were left and right circularly polarized, respectively. This was achieved by inserting appropriately oriented quarter-wave retarders. In this setup the intensity is constant over the entire area of the film, but the resultant linear polarization is periodically modulated.⁷ The j th diffracted order arising from the incident beam I_i is denoted by $I_{i,j}$. Thus $I_{1,+1}$ denotes the order +1 arising from I_1 . The incoherent blue source was obtained by passing the light of a Xe lamp through a bandpass filter (350–450 nm) and focusing the resulting beam onto the film, giving a power of about 30 mW/cm^2 . In order to follow the evolution of the diffraction efficiency of the recorded gratings, the first order diffracted power of a vertically linearly polarized 780 nm diode laser (30 mW) was measured with a Si detector. It was confirmed that the light coming from the 780 nm laser had no influence on the recording process and subsequent evolution of the gratings.

Figure 2 shows the 780 nm diffracted power as a function of time for a polarization grating recorded in a P6a4 film. At $t=0$ s the blue light of the Xe lamp was made to fall upon the sample. No diffraction was observed before and during irradiation with the Xe lamp although a noticeable increase in the transmission was observed after the blue illumination period. This increase in transmission was ascribed to changes in the morphology of the polymer since the fine-grain texture observed before blue irradiation disappeared.¹⁹ The disappearance of the morphology can be ascribed to the *trans-cis* isomerization, as the *cis* states do not form liquid crystalline phases. At $t=600$ s the Xe lamp was switched off and the two He-Ne beams were made to interfere on the

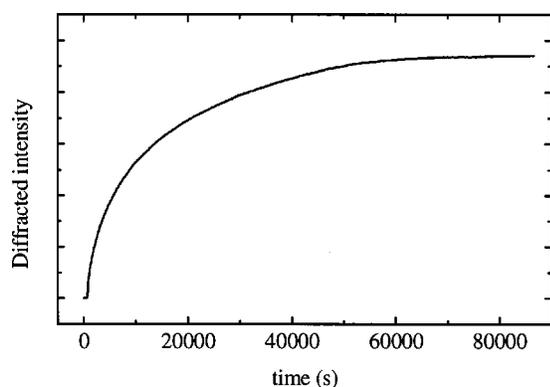


FIG. 2. Diffracted intensity of the 780 nm laser as a function of time. At $t=0$ s, blue light and light of 780 nm are turned on; at $t=600$ s the blue light is turned off and two He-Ne beams (left/right circularly polarized) are turned on; at $t=900$ s the He-Ne beams are turned off.

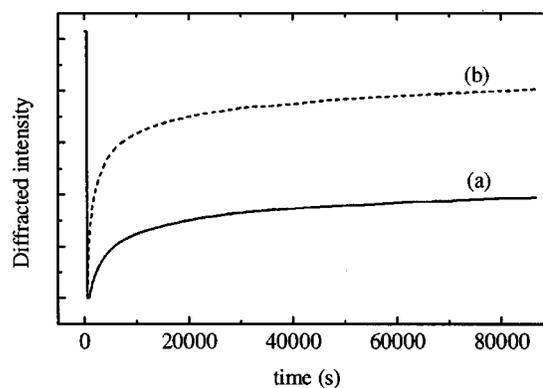


FIG. 3. Curve (a) represents the decrease and the recovery of the 780 nm intensity diffracted by a previously recorded grating. At $t=0$ s only the 780 nm light is on. At $t=600$ s the blue light is turned on; at $t=610$ s the blue light is turned off. Curve (b) was obtained in a similar way to (a) but a circularly polarized He-Ne beam was allowed to fall upon the film after $t=610$ s.

film. After a short time (about 30 s) the 780 nm diffracted intensity started to grow. At $t=900$ s the He-Ne laser was switched off. The diffracted power kept on increasing for several hours until it reached a saturation value.

In order to confirm that we had indeed produced a polarization grating, the diffraction selectivity of the film towards circularly polarized light was measured.⁷ The circularly polarized I_1 beam from the He-Ne laser was allowed to fall upon the grating after the film had reached its efficiency saturation value. We did not observe, at this stage, any influence of the He-Ne light on the behavior of the grating. When we measured the diffraction efficiency, defined as the ratio between the $I_{1,+1}$ diffracted intensity and that of the incident beam I_1 , we obtained a value of 29%. An efficiency of about 0.25% was obtained for the $I_{1,-1}$ diffracted beam. The marked contrast between these two diffracted beams shows (see Ref. 7) that our grating is mainly a polarization one associated with a periodic modulation of the molecular orientation along the grating vector direction. Besides, as mentioned above, the diffraction efficiency obtained in our films is more than two orders of magnitude higher than those previously reported for other azobenzene-containing systems in conjunction with biphotonic holography.

The formation of holographic polarization gratings by means of biphotonic processes in liquid crystalline polymer films has been discussed previously.^{14–16} Blue illumination of the film generates a stationary population of *cis* molecules. Subsequent illumination with red light induces *cis-trans* transitions and it has been demonstrated that *trans* molecules are preferentially aligned parallel to the polarization direction of the red light. This fact forms the basis of biphotonic polarization holographic recording. Growth in darkness has been ascribed to intermolecular interactions between adjacent mesogenic molecules that gives rise to cooperative effects in the liquid crystalline phase.^{15,16}

During the course of this study we also investigated the erasure of the generated gratings. Curve (a) in Fig. 3 shows the evolution of the diffracted intensity during and after the erasing process. We began our experiment with a high efficiency grating. At $t=0$ s only the 780 nm beam was present and a high diffracted power was observed. At $t=600$ s the

blue light was switched on for 10 s and the diffraction intensity dropped to zero. The sample was then left to evolve in darkness and, after some time, a partial recovery of the diffraction efficiency (about 35% of the initial value) was observed. Curve (b) in Fig. 3 represents a similar experiment but with the presence of a circularly polarized He–Ne beam after the 10 s period of blue light illumination. An increase in the recovery rate and a higher recovered intensity (up to 75% of the initial value) were observed in the presence of red light.

If the erasure of the grating was produced by long periods (several hours) of blue light irradiation, no memory of the previously recorded grating was observed. Similar erasure without recovery can be achieved by thermal treatment at 80 °C during several minutes followed by cooling the sample to room temperature.

Optical anisotropy in the P6a4 side-chain polymer is mainly due to the orientation of azobenzene pendant chromophores. Blue light destroys this orientation through *trans*–*cis*–*trans* isomerization processes. This process gives rise to rapid erasure of the polarization grating. However, some kind of latent polarization grating, which does not give rise to any detectable diffraction, must remain in the film after this erasure. This latent grating would provide the seed for the subsequent recovery of the diffracted power. The origin of this latent grating is not clear but it could be due to some orientation of the polymer main chain during production of the grating. Long blue-light erasure times or high-temperature annealing of the film would destroy this latent grating. The influence of red light in the recovery process could be associated with the increase in the rate of *cis*–*trans* isomerizations induced by the red light.

In conclusion we have described the recording of polarization gratings in the azobenzene polyester P6a4 by means of biphotonic processes using incoherent blue light from a Xe lamp and the coherent red light from a He–Ne laser. Diffraction efficiencies that are two orders of magnitude higher than those previously reported have been achieved. Partial recovery of the diffraction efficiency has been ob-

served after the disappearance of the diffracted light under blue illumination for a few seconds. This memory effect has been tentatively ascribed to orientation of the polymer main chain during the creation of the grating.

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