

Bi-photonic transient gratings in bulk azo-dye containing poly(methyl methacrylate) matrix

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Amorphous bulk composites were prepared by doping azo-dye disperse red 1 (DR1) in poly(methyl methacrylate) (PMMA) matrices. Photoinduced anisotropy of such kind of bulk polymer material was investigated experimentally by measuring the dichroism when irradiating with linearly polarized green light with different polarization direction. With the interaction of bi-photonic beams at 514 and 632.8 nm, transient gratings in the bulk composites could be established, which was a kind of population gratings of trans and cis DR1 isomers and was attributed to the weak absorption of cis isomers at 632.8 nm and the positive dichroism of trans isomers at 514 nm. Furthermore, the all-optical switching behavior of the transient holographic gratings was observed repeatedly by turning on and off the writing beams and a response time of ten milliseconds order could be obtained.

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Integrated optical micro-devices require the development of the holographic technique for the realization of lens matrices, prisms, and diffraction gratings of micrometric dimensions. Both permanent and transient holographic systems find important applications in this field. Materials containing photo-responsive dyes have been found to be suitable for such a task and therefore become attractive in the field of optical communication and high-density optical data storage^[1-4]. Azo-dye containing polymers are usually known for the large photoinduced linear birefringence that makes them attractive for reversible optical storage and other optical applications^[1,5]. It has now been generally accepted that the photoinduced anisotropy of such materials is a consequence of the reversible trans-cis photoisomerization with respect to the N=N double bonds of the azobenzene groups, which induces an angular redistribution in the orientation of the photochromic entities^[6]. Because of the selectivity of excitation, the chromophores will tend to orient in a direction perpendicular with respect to the polarization of the actinic light, which leads to photo-induced birefringence, dichroism and even mass transport^[1-4]. Various azo-dye molecules in Langmuir-Blodgett (LB) molecular films^[7], liquid crystalline thin films^[8], and amorphous polymer films^[5] have been intensively investigated for the applications in photonic devices, especially in holographic recording^[9,10]. Comparing with the azo-dye containing films, bulk materials have inneglectable thickness and the photophysical mechanism of the chromophores is important in the three-dimensional optical storages, optical waveguides, and other nonlinear optical applications^[11-13].

In this paper, azo-dye doped polymer bulk with several millimeters thickness was prepared. The photoinduced dichroism in the bulk was studied and based on the weak absorption of the cis isomers in long-wavelength, we presented a type of population gratings of trans and cis isomers in the bulk material which operated under

two color lights, a short-wavelength light from an Ar ion laser, a long wavelength light from a He-Ne laser. Though such similar biphotonic holographic gratings in thin films have been reported^[14-16], it was reported at first time in azo-dye containing bulk polymer. And the potential applications of this transient gratings in all-optical switches were demonstrated at last.

The poly(methyl methacrylate) (PMMA, $M_w=93000$) and the disperse red 1 (DR1) were purchased from Aldrich Chemical Company. The detail of the sample preparation is similar to that described in Ref. [17]. At last, the bulk PMMA samples containing about 0.1 wt.-% of DR1 were obtained. The glass-transition temperature of the composites was about 104 °C and the absorption spectrum of the sample is shown in Fig. 1. A 10 × 10 × 3 (mm) parallelepiped with thickness about 3 mm was cut out of this polymeric block. The two opposite faces with an area about 10 × 10 (mm) were polished and used as sample surfaces.

Figure 2 illustrates the geometry used for observing the photoinduced dichroism in the bulk polymer sample. An

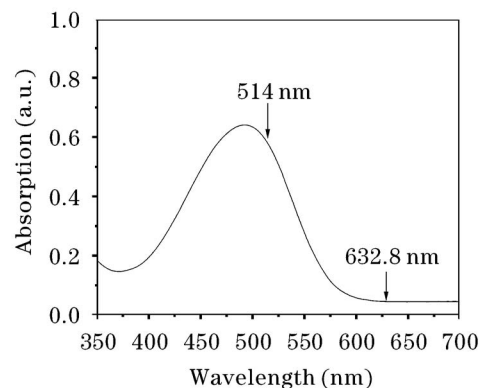


Fig. 1. The absorption spectrum of DR1 doped PMMA bulk polymer.

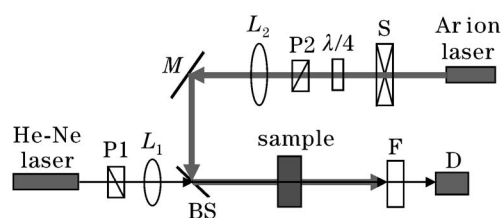


Fig. 2. The setup for the dichroism measurements. S: shutter; $\lambda/4$: wave plates; P1, P2: polarizers; L_1 , L_2 : lenses; M: mirror; BS: beam splitter; F: filter; D: detector.

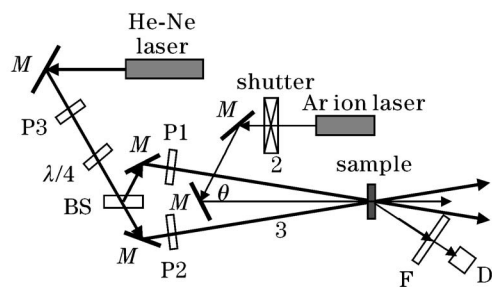


Fig. 3. Holographic recording setup.

argon ion laser beam (514 nm, with a diameter of 2 mm) was used as the pump beam. The sample was placed after a polarizer P1 in the path of a He-Ne laser beam (632.8 nm, probe beam, with a diameter of 0.5 mm). By rotating P2, the polarization direction of the green light could be changed and a $\lambda/4$ wave plate before P2 was used to keep the intensity almost the same in different polarizations. The optical change of the sample induced by pump beam was monitored by detecting the intensity of the probe beam transmitted through the sample. A filter with an absorption bandwidth centered at 514 nm was placed in front of the detector (also in Fig. 3) to remove all the transmitted or scattered light coming from the Ar ion laser. The transmitting intensity (in Fig. 2) and the first order diffracted He-Ne signal (in Fig. 3) were automatically recorded with a photomultiplier tube and a high speed digital oscilloscope (Tektronix, TDS-3032 model).

Another experimental setup used for investigating the holographic characterization of the bulk sample was presented as shown in Fig. 3. The red light at 632.8 nm from a He-Ne laser was split into beam 2 and beam 3 by a beam splitter. Using a $\lambda/4$ wave plate and polarizers P1, P2, and P3, beam 2 and beam 3 with S polarization and nearly equal intensity could be obtained. With a crossing angle about 6° , beam 2 and beam 3 overlapped in the PMMA bulk with a crossing area about 3 mm in diameter, where it was overlapped by a linearly polarized 514-nm beam with an area about 4 mm in diameter from a continuous wave (CW) Ar ion laser. The polarization of 514-nm beam could be changed by the wave plate and polarizer, which were not shown in Fig. 3. The Ar ion laser beam was controlled by a shutter.

The photoinduced dichroism is a property that shows the photoinduced anisotropy in the sample. The experimental setup was shown in Fig. 2. The intensity of the probe and the excitation beams were about 20 and 636.6 mW/cm², respectively. Figures 4(a) and (b) show the changes in transmission of the probe beams under the

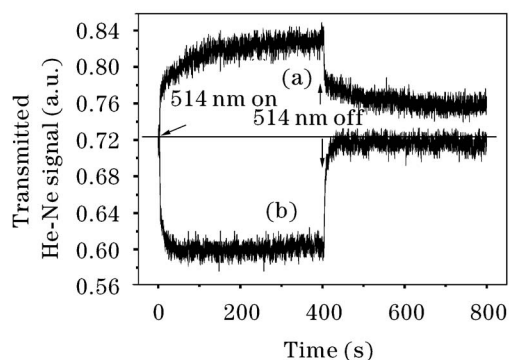


Fig. 4. The photoinduced dichroism of the bulk sample when the polarizations of the beams are parallel (a) or perpendicular (b).

irradiation of the pump beam polarized parallel and perpendicular to the polarization direction of the probe beam, respectively. As one can see that the results were quite different in these two cases. After the excitation beam at 514 nm was switched on, obvious increase and decrease in the transmission of the probe beam could be observed in these parallel- and cross-polarization geometries. When the excitation beam was switched off, the transmission of the probe beams in these two cases tended to return to their initial value. It should be noted that after the excitation beam was removed, the probe's transmission in the perpendicular case was almost the same as before excitation. While in the parallel case an additional increase in transmission was still remained. Different from the results described in Ref. [12], the rapid increase and decrease jumps of transmitted signal, which came from the excitation of the trans and cis populations to excited singlet and triplet states at the moments of switching on and off the pump light, were not observed in our experiments. Furthermore, obvious increase of the probe's transmission in steady-state excitation regime in the parallel case could be observed in our experiments. However, in Ref. [12], the probe's transmission was almost the same as before excitation in the parallel case.

It is well known that there exist two kinds of isomers, the trans and cis isomers, of azo-dye molecules^[6]. To the dye we used here, the trans form is more stable at room temperature than the cis form. And the experiments showed that the cis isomer had stronger absorption at the probe wavelength than that of the trans isomer^[10,12]. In addition, the trans isomer had positive dichroism which led to a higher absorption when the light polarization was parallel to the dipole moment of the dyes^[12]. As the excitation beam was turned on, cis isomers were generated and then some cis isomers isomerized back to trans form. And the steady-state excitation of the sample led to the combination of cis and reoriented trans forms (the molecular geometrical axis perpendicular to the pump beam polarization direction^[6,9]). The appearance of cis isomers increased the absorption of the probe beam and decreases its transmission. The transmission decrease was more significant for the cross-polarized probe because it was accompanied by reorientation of the trans forms. More trans isomers with their long molecular axes orientation parallel to the polarization direction of probe beam appeared, which enhanced the absorption of

He-Ne beam because of the positive dichroism of trans molecules. Thus the cross-polarized probe transmission in the steady-state excitation condition was reduced significantly below its initial value (Fig. 4(b)). While in the parallel pumping case, the polarization directions of pump and probe beams were the same. After the pump light was on, the population of trans in the polarization direction of the probe beam was depleted. Though the appearance of cis isomers increased the absorption of He-Ne light, the absorption from the positive dichroism of trans isomers decreased drastically, which increased the probe's transmission at last. Some of the oriented chromophores could not return to their initial random orientation state after the pump beam was off, which led to the result that the transmission of He-Ne beam could not reach to their initial value.

Figure 5 shows the transient gratings recording in the bulk sample. Different from the usual holographic recording in azo dye containing materials in which short wavelength such as blue or green light was usually used as recording beams, two He-Ne laser beams were chosen as the writing beams and the 514-nm light of Ar ion laser as another pump beam in our experiment. When only the two He-Ne beams (beam 2 and beam 3 in Fig. 3) with nearly equal intensity and S polarization overlapped in the bulk sample, no diffracted He-Ne signal could be observed, as shown in Fig. 5(a). As the 514-nm beam was turned on, weak diffraction of He-Ne light could be detected. With the same pumping intensity of 514-nm light, we changed the polarization direction of 514 nm parallel and perpendicular to that of the He-Ne light and investigated the dynamic processes of the transient gratings in the bulk sample. Figures 5(b) and (c) show the dynamic behavior of diffracted He-Ne light in the perpendicular and parallel cases, respectively.

When only two He-Ne beams with S polarization direction overlapped in the sample, a spatial-intensity interference field with S polarization in the bright red fringes could be obtained. As the linearly polarized green beam was switched on, the trans isomers oriented in the same direction with green light were excited in much larger possibility and some cis isomers were generated in the green light irradiation area. The cis isomers in the bright red fringes could be excited and isomerized back to the trans form until the trans molecules were oriented in the direction perpendicular to the He-Ne light polarization

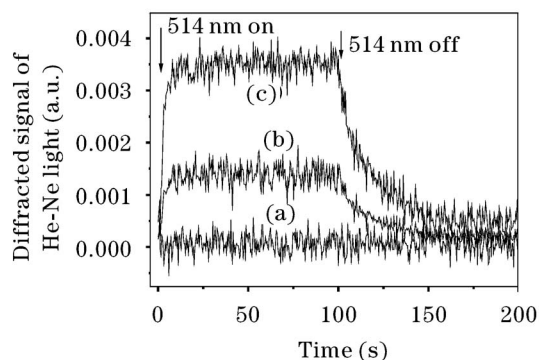


Fig. 5. The transient gratings in bulk sample. Without the 514-nm beam pumping, no diffracted He-Ne signal can be detected (a). Curves (b) and (c) show the diffracted He-Ne signal in orthogonal and parallel pump cases, respectively.

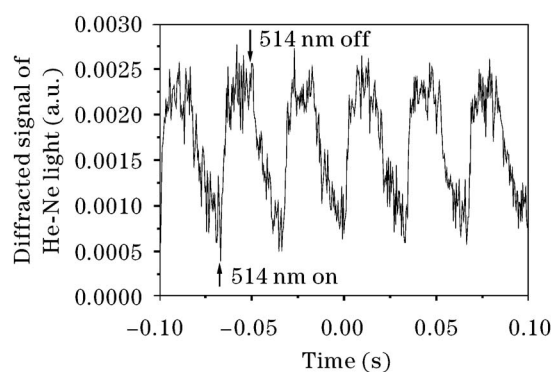


Fig. 6. The switching effect of the bi-photonic transient gratings in bulk samples.

direction. So a kind of population gratings of trans and cis isomers was established in the bulk and the diffraction of He-Ne beam could be observed. Generally, the cis isomers in the black red fringes would isomerized back to the trans isomers at room temperature, and after some trans-cis reaction cycles the trans form in these regions would reach to a state with their long molecular axes perpendicular to the green light polarization direction. And this would at last weaken the popular gratings and decrease the diffracted signal of He-Ne light^[10]. But in our experiments, such decrease in diffraction was not observed. We thought that because of the different molecular environments and steric interactions between dye molecules and polymer matrix, it was impossible for all chromophores to reach a complete orientation. So always part of chromophores took part into the trans-cis isomerization cycles and in equilibrium state the stable population gratings of trans and cis isomers could remain. As shown in Figs. 5(b) and (c), the diffracted signal of the parallel pump case was larger than that of the perpendicular case. In the perpendicular pump case, more chromophores with their molecular axes parallel to the polarization direction of the He-Ne light were accumulated in the bright red fringes and the additional absorption from the positive dichroism of the trans isomers decreased the diffraction signal of the He-Ne light.

In Fig. 6, we show the optical switching effect of the first diffraction efficiency in the bulk samples. The green light was chopped by a mechanical chopper and the modulated diffraction intensity of the He-Ne beam is obtained. From Fig. 6 we can see that, the response time of the bi-photonic transient gratings in azo-dye doped PMMA bulk is about several ten milliseconds, which is much faster than the recently reported results of transient gratings in azo-dye containing liquid crystal (LC) films (about 150—190 ms)^[18]. Such kinds of transient gratings should have great potential use in all-optical communication device.

In summary, we have studied the photoinduced dichroism in the DR1-doped PMMA bulk material based on the photoinduced isomerization and reorientation of azo-dye chromophores. In our dichroism experiments, the trans isomer showed higher absorption when the probe light polarization was parallel to the molecules' long axis (positive dichroism of trans isomers), though generally the absorption of the probe light was stronger in the dye's

cis isomer. Taking into account the weak absorption of cis isomers and the positive dichroism of trans isomers in 632.8-nm light, a kind of transient population gratings of trans and cis isomers could be established in the bulk sample with the interaction of a 514-nm light and a intensity interference pattern of 632.8-nm light. This kind of transient two-color gratings is firstly reported in bulk samples and may be useful in application for optical information processing.

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