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# Nonvolatile grating in an azobenzene polymer with optimized molecular reorientation

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We demonstrated a nonvolatile grating using an azobenzene polymer film with polarized two color beams. The reorientation of azobenzene molecules can be optimized when the two color light beams are polarized perpendicularly. The stored information can be read repeatedly without volatility with the same wavelength as the writing beam. © 2001 American Institute of Physics.

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Molecular orientation controlled by light is useful for many applications such as display and information storage.<sup>1–6</sup> Small molecular size permits high spatial resolution. Holographic data storage is an attractive technique because of its extremely high capacity, fast data access, and exceptionally fast data transfer rate.<sup>7–9</sup> However, the stored information can be easily erased by reading with a wavelength close to the writing. Nonvolatile holographic storage is achieved in inorganic crystals doped with two centers.<sup>10–12</sup> In this letter we report a nonvolatile grating based on optimizing molecular reorientation of a photoisomerized azobenzene thin film by using polarized light beams of two colors. The azobenzene organic chemical is inexpensive and commercially available. Optical quality thin polymer films of the material with large area can be easily prepared. Polarized blue color light is used to generate trans–cis isomerization and molecular reorientation. A red beam causes cis–trans isomerization, which optimizes effectively the reorientation when the red light is polarized perpendicularly to the blue light. This feature enables transfer of a volatile isomerization grating to a nonvolatile molecular reorientation grating. Our results show the stored information can be read repeatedly for 12 h without volatility by using a beam with the same wavelength as the writing beam.

The molecular photoinduced reorientation usually takes place in fluid systems such as liquid crystals. However, the azobenzene derivatives can be oriented in solid matrices by polarized light due to the accompanying process of trans–cis–trans isomerization.<sup>4,5</sup> The trans azobenzene derivatives are stable with an elongated molecular form and the cis azobenzenes are photoinduced isomers with a bent form and revert back to trans form thermally or by light. The length of azobenzene part of the derivatives is about 1.0 nm for the trans form but only 0.56 nm for the cis form.<sup>13</sup> This remarkable change of molecular dimension results in the bent cis form rotating more easily than the trans. Electron push–pull substituents such as parador and para'acceptor enhance the reorientation anisotropy of the azobenzenes. In some matri-

ces of bulk polymers, after blocking light, reorientation of the azobenzene molecules can be frozen below the glass transition temperature ( $T_g$ ) due to the restriction of free volume of the polymer to the movement of the trans molecules.<sup>5,6</sup> We used a thin polymer film of poly(vinyl alcohol) (PVA) doped (1% by weight) with an azobenzene of 4-[4-(dimethylamino)-phenylazo]benzenesulfonic acid, sodium salt. The linear absorption of the azobenzene (trans form) shows a broad absorption band centered around 450 nm due to  $\pi \rightarrow \pi^*$  transition. Beyond 600 nm the film is transparent. Under irradiation with blue light, the spectrum shows a small absorption beyond 600 nm due to the photoinduced cis isomer. The PVA polymer with average molecular weight of 124 000–186 000 is transparent in the visible region. Both chemicals are water soluble. To get a good homogeneous mixture, we stirred the mixed solution for 2 h after pouring the azobenzene powder into the PVA solution which was dissolved with distilled water and also stirred for 2 h. The homogeneous mixed solution was coated on an optical glass substrate. The entire process of the film preparation was conducted at about 85 °C close to  $T_g$  temperature of PVA polymer. The thickness of the polymer film is about 10  $\mu\text{m}$ .

We performed the experiment of photoinduced anisotropy by use of polarized exciting beams of two colors to investigate the features of optimization of reorientation of the azobenzene molecules. The sample is placed between two crossed polarizers (vertical and horizontal) and a weak He–Ne 633 nm beam (10 mW/cm<sup>2</sup>) is used to probe the photoanisotropy of the sample. Initially no light reaches the detector due to the random distribution of the azobenzene molecules. When an exciting beam polarized at 45° to the vertical from a 442 nm He–Cd laser irradiates the sample, the analyzer transmits some 633 nm light. This photoinduced anisotropy is due to the reorientation of the azobenzene molecules induced by the 442 nm light. The azobenzene transition moment lies along the molecular axis and only the molecules with their orientation parallel to the electric vector absorb light. The repeated trans–cis–trans isomerization results in the alignment of azobenzene molecules in the direction perpendicular to the polarization of the exciting beam. We observed that the molecular reorientation can be opti-

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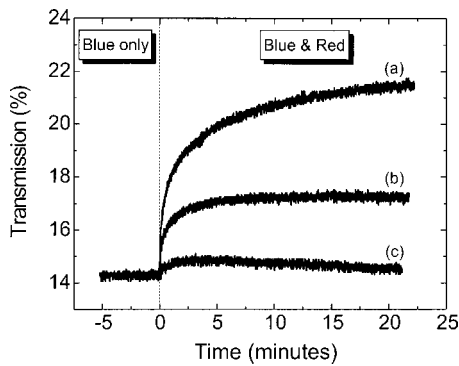


FIG. 1. Photoanisotropy experiment in poly(vinyl alcohol) film doped with 4-[4-(dimethylamino)-phenylazo]benzenesulfonic acid, sodium salt, by using two color exciting beams with different polarizations. After the photoanisotropy induced by a 442 nm blue beam ( $180 \text{ mW/cm}^2$ ) polarized at  $45^\circ$  to the vertical reaches the saturable value, we turn on the red 647 nm exciting beam ( $2.2 \text{ W/cm}^2$ ) polarized (a) perpendicularly, (b) circularly, and (c) parallel to the blue beam.

mized by using another beam of long wavelength. To prevent any absorption by the trans isomers, we use a red 647 nm beam from Ar–Kr ion laser to irradiate the sample counter to the direction of the blue beam. When the red beam is polarized perpendicularly to the blue beam, the photoinduced anisotropy by the polarized blue light will be enhanced greatly. The results are shown in Fig. 1. With circularly polarized red beam, the photoanisotropy is also increased but the value is less than in the former case. With the red beam polarized parallel to the blue beam, the enhancement is very small. The mechanisms of optimizing molecular reorientation are illustrated in Fig. 2. When the film is irradiated only by the blue beam, the azobenzene distribution shows a mixture of trans and cis form oriented perpendicularly to the blue light polarization due to repeated absorption of trans and cis isomers with their axes oriented in any direction not cross to the blue polarization. The molecular anisotropy depends on push–pull substituents in 4- and 4'-(para and para') positions, respectively. In the trans linear form the substituents are on the molecular axis enhancing the delocalization of the  $\pi$  electrons. On the other hand, in the bent cis form the substituents are situated off the molecular axis decreasing the anisotropy. However, if the red exciting beam polarized parallel to the direction of cis transition moment also irradiates the sample, the cis isomers will isomerize back to the trans form by absorbing the red light. The trans isomers will absorb blue light again if their axes are not perpendicular to the blue light polarization, until all molecules become trans form with their axes in the direction of

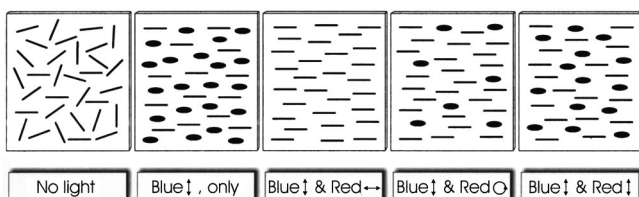


FIG. 2. Schematic illustration of optimizing reorientation of the azobenzene molecules induced by linearly polarized blue light as well as by a combination of polarized blue and red beams. The strip represents trans isomers absorbing blue light and the ellipse represents cis isomers absorbing red light.

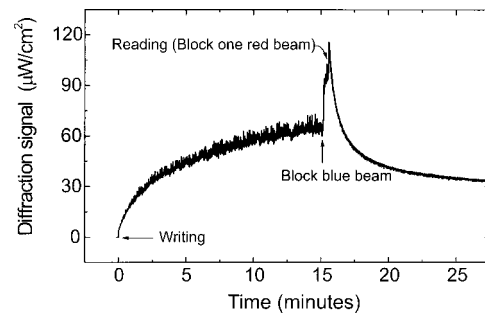


FIG. 3. Temporal evolution of grating recording and grating readout. Two *s*-polarized 647 nm beams with equal intensity of  $150 \text{ mW/cm}^2$  are to form grating. *p*-polarized 442 nm light with total intensity of  $60 \text{ mW/cm}^2$  results in trans-to-cis isomerization and reorientation. Before beginning to write the grating, the film was preexposed by a circularly polarized 442 nm light for 2 min. At  $t=0$ , turn on two red writing beams and change the blue light to *p*-polarized;  $t=15$  min, block the blue beam; then after 25 s, block one red beam and begin to read.

the red light polarization. The elongated trans isomer does not absorb red light and exhibits much larger anisotropy than the cis isomer. The circularly polarized red light also optimizes the reorientation but not thoroughly. For the case where the red light is polarized parallel to the blue light, there is no significant improvement in the reorientation because the cis isomers do not absorb the red light polarized perpendicularly to their axes.

This feature of the optimization of molecular reorientation offers an interesting possibility for the sample to store and read information using coherent light with the same long wavelength without volatility. We exploit this in the experiments of holographic storage. Two *s*-polarized coherent beams from an Ar–Kr ion laser at 647 nm intersect on the surface of the azobenzene film with an angle of about  $5^\circ$  to form the holographic grating. The sample is also irradiated by 442 nm light from both sides of the film in order to bring about uniform trans–cis isomerization and preorientation. The blue beam need not be coherent. An incoherent light source with short wavelength can be used in the experiments. We detect the first-order signal of self-diffraction (read by its writing beams) with a photodetector. To ensure an initially random distribution of the molecules, the film is preirradiated for 2 min by a circularly polarized blue light before writing the grating. Then, we change the blue light polarization and turn on the red beams. We observe that the signal intensity depends significantly on the polarization of the blue light. By using *p*-polarized blue beam, the signal intensity is about eight times larger than that by using the *s*-polarized beam. The reason for this can be understood from Fig. 2. The azobenzene molecules located in the dark fringes of red interference field are aligned only by the polarized blue light. However, the molecules in the red bright fringes are aligned by both blue light and red light. As the reorientation is optimized more efficiently by additional red light polarized perpendicular than parallel to the blue polarization, the reorientation grating with the *p*-polarized blue light is more intense than that with the *s*-polarized. Figure 3 displays the result with the *s*-polarized red beams and the *p*-polarized blue beam. It is shown that the signal increases after turning on the writing beams. When blocking the blue light, the signal quickly increases because there exists an enhanced isomer-



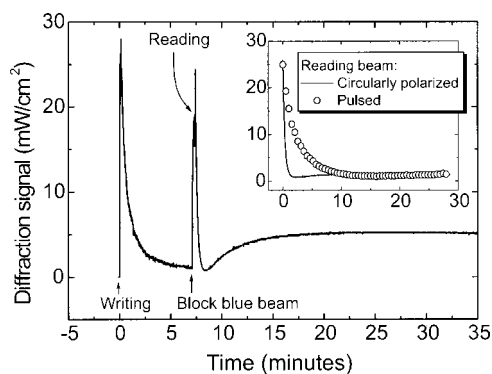


FIG. 4. Grating recording and renewal by the reading beam with *s*-polarized red and blue beams. Before writing grating, a circularly polarized blue beam preirradiated the sample for 2 min. Then turn on the red writing beams and change the blue light to *s*-polarized. The inlaid figure shows reading process using a circularly polarized red beam and an *s*-polarized red pulsed beam with 1 s exposure and 30 s delay. The intensity of red beams is  $300 \text{ mW/cm}^2$  for each beam and the blue beam is  $60 \text{ mW/cm}^2$ .

ization grating in which the cis isomers in bright red fringe isomerize further back to the trans form due to the termination of trans-to-cis isomerization.<sup>14</sup> The response of the weak isomerization grating is fast but it is usually buried by the reorientation grating. Moreover, the isomerization grating cannot last long due to the limited lifetime of cis isomer. After the isomerization grating reaches its maximum, we block one red writing beam and use another red beam to read the grating. The results show another immediate increase as the grating read by one beam gives higher diffraction efficiency than when it is read by two beams. The two beam geometry corresponds to self-diffraction, in which one beam may erase the grating while the other beam acts as reading beam. Afterwards, the diffraction signal decreases as a result of the erasure of isomerization grating induced by the uniform red reading beam. Once the isomerization grating is completely erased, the remnant reorientation grating is stable. Our results show this grating can be read repeatedly for 12 h without obvious attenuation by using 647 nm beam with an intensity  $200 \text{ mW/cm}^2$ . Additionally, the reorientation grating can be easily erased by a circularly polarized blue or UV light or by heat. Similar results are obtained if we use circularly polarized blue light instead of *p*-polarized, but the signal intensity is lower in this case.

Figure 4 shows the results of the grating formation and readout by using both *s*-polarized blue and red beams. It is found that the diffracted signal exhibits a peak (as fast as 1 s) when the writing beams are turned on. We believe the formation of the initial diffraction peak is due to the isomerization grating. The blue light causes the trans azobenzene molecules to isomerize to the cis form with the same molecular orientation because the photoisomerization process is much faster than the molecular reorientation. Since the red light exists at the same time and its polarization direction is parallel to the cis molecular axes, the cis-to-trans isomerization will occur immediately in the bright fringe area and result in an isomerization grating. After the molecular reorientation begins, the molecular population with their axes in the direc-

tion of the blue light polarization decreases; as such the intensity of the diffracted light from the isomerization grating decreases. The isomerization grating depends on the polarization of the preirradiated blue light. The preirradiation using *p*-polarized blue light results in the largest initial peak, and with *s*-polarized preirradiation there is almost no initial peak. The reason is the *p*-polarized blue light provides more initial cis isomers in the direction of red *s*-polarization than the *s*-polarized blue light before writing the grating. Figure 4 also shows that when the blue beam is blocked, the diffracted light from the isomerization grating increases again due to the same fact in Fig. 3. After the signal reaches a maximum, we stop writing and use a red beam to read the grating. It is interesting that we observe a grating renewal effect induced by the reading process. This feature is observed when the red intensity is more than  $200 \text{ mW/cm}^2$ . Due to the destruction of the isomerization grating, the signal decreases fast at the beginning. However, the grating will be enhanced magically after the signal almost disappears. We use read beams of different polarizations to investigate this interesting feature. It is found that only the *s*-polarized read process brings the enhancement. Additionally, the grating will simply decrease to a value with the cis lifetime when we use short pulses to read to avoid erasure. We conclude that this grating renewal originates from realignment of the remanent cis isomers (in dark fringe before) by the *s*-polarized read beam during the cis-to-trans isomerization process. The resulting trans isomers in the dark fringe (before) exhibits a trend of *s*-direction reorientation induced by the uniform *s*-polarized red beam but no change in the bright fringe (before) where the molecules are already turned to *p*-direction induced by the *s*-polarized blue beam. As a result, a new reorientation grating is formed by the reading beam.

The advantages of this technique are that small diode beams can be used for the coherent red light and the same wavelength can be used for both writing and reading without additional electric field. The technique we demonstrated for optimization of molecular reorientation may also be useful for other applications such as optical display, information processing, and enhancement of second order nonlinearities.

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