Azodye gelatin films for polarization holographic recording

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ABSTRACT

Mordant Pure Yellow azodye in a matrix of gelatin is proposed as a media for stable polarization recording. Relatively high values of birefringence are measured (over $\Delta n = 0.02$). Polarization diffraction gratings are recorded with two circularly polarized waves and diffraction efficiency of 67% is achieved at 633nm. Protected from the humidity, the recording is stable. Long term radiation by 633nm probe beam is harmless as well. Unusual behavoiur is observed when acting on the recorded grating alternatively with one of the recording beams. The left circularly polarized beam erases the grating sharply, while the right circularly polarized beam, before erasure, first increases the diffraction efficiency.

Keywords: azodye, azo-dye, polarization holography, polarization diffraction grating, circular analyzer

1. INTRODUCTION

Many studies have been dedicated to the optical recording in azodye based systems. Since these materials have very large values of the photoinduced anisotropy, they are suitable for the aims of modern optics and information and telecommunication technologies, optical recording and processing, interconnectors in computers, etc. It is known that trans-cis isomerisation of the molecules of azodyes occur under the action of polarized light. This leads to reversible ordering and/or reorientation of the molecules. As a result optical anisotropy arises which is the base for producing polarization elements, holographic polarization gratings, etc. By choosing different type of azodyes solved or covalently bounded to different polymer matrices, it is possible to achieve different values of the photoanisotropy sensitivity, as well as stability/reversibility of the recording. Here we report the investigations of the birefringence induced in films of Mordant Pure Yellow (MPY) azodye dissolved in a matrix of gelatin. The ability to produce stable polarization gratings on the basis of this media is also investigated. As is known, two main types of polarization gratings could be recorded in a material which possesses photobirefringence and dichroism with two orthogonal linear polarizations or with two circular polarizations — left and right. The second case is more interesting because such gratings have the unique polarization property which is not found among conventional optical elements. These gratings split the entering light into two diffraction orders. The intensity of each order is proportional to the part of left or respectively right circularly polarized component of light. Thus, if a linear polarization enters, the intensity in the two diffraction orders will be equal. If a circular polarization enters there will be only one diffraction order (apart from the zeroth one). It was shown that such gratings could be used as circular polarization analyzers[1] and a device for simultaneous measurement of all Stokes parameters of light in real time, was proposed[2]. But recently it was found that holografic gratings recorded in azodye containing materials, as a side effect, acquire

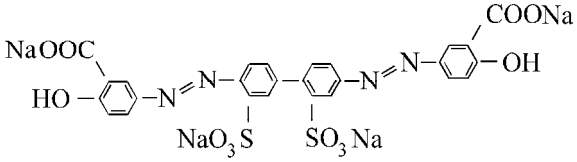

Fig. 1. Mordant Pure Yellow structure

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surface relief[3]. The surface relief spoils the polarization property of the transmission grating as a circular analyser and thus is unwanted. Relief was observed even in the case of polarization recording, where the interference pattern on the sample is only polarization modulated while the intensity is uniformly distributed[4]. Thus the problem to have stable polarization gratings is to find a material which has a relatively high photo-birefringence, does not aquire relief and has a long lasting memory.

2. SAMPLES

The dye — Mordant Pure Yellow is a bis azo dye (fig. 1). Searching among the abstracts in 18,000 journals in the Uncover database gives only 5 articles for Mordant yellow, only 2 of which are optics related[5,6] Both are dedicated to the guest host system MPY/Polyvinylalcohol. The anisotropy in this system disappears in darkness and room temperature for several minutes. This is because the reoriented molecules easily come back to their original positions without substantial resistance from the polymer matrix. Since the dye is water soluble another possible choice for the matrix is gelatin. This unique natural product is known for many years with its remarkable properties and still has no analog in traditional photography. That is why we used industrial quality photo plates as a base for our samples. Any type of photo plate could be used but we find that for the long memory effect, fine grain, such as astroplates and holographic plates, are preferable. The plate is put in a fixing solvent to remove the silver chloride particles. After that we have a gelatin emulsion which is ready to accept the dye. It is put in a saturated water solution of MPY for 15 min, after which it is dried. The films are 20 μm thick and have good optical quality. For the lasers we used the transmission of our samples is T_{488}=0.5% and T_{633}=79%, respectively.

3. EXPERIMENTAL SETUP

Linearly polarized Ar^+ beam with λ=488nm induces the anisotropy, while the probe beam is comes from a He–Ne laser, λ=633 nm.

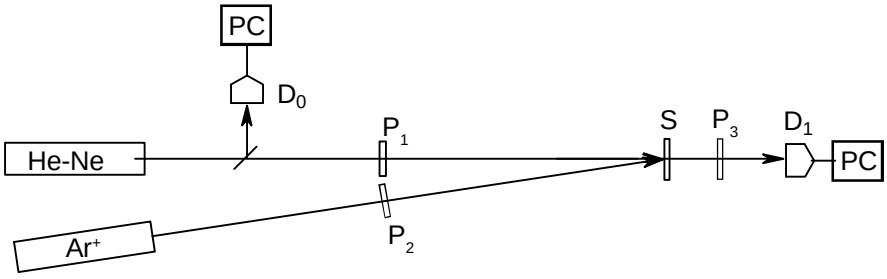

Fig. 2. Experimental Setup. P_i – polarizers, D_i – photo-detectors, S – sample

The angle between pump and probe beam is well below 5^0. D_1 is the main photodetector and D_0 is to control and normalize the intensity of the measuring beam. P_1,P_2 and P_3 are polarizers. The Ar^+ beam has an intensity of 30 mW and vertical polarization. The probe beam is 2mW and polarized linearly under 45^0. Polarizer P_3 is set parallel to P_2. The sample could be described as a linear retarder with a vertical fast axis by the Jones matrix:

$$M = \begin{vmatrix} \cos\left(\frac{d}{2}\right) - i\sin\left(\frac{d}{2}\right) & 0 \\ 0 & \cos\left(\frac{d}{2}\right) + i\sin\left(\frac{d}{2}\right) \end{vmatrix} \quad (1)$$

where δ is the phase difference induced between the vertical and horizontal components of the probe beam. After some calculations we obtain a quadratic cosine formula describing the normalized signal intensity at D_1.

$$J_1 = \cos^2\left(\frac{d}{2}\right) \quad (2)$$

Thus the signal curve during the excitation will be maximum in the begining (parallel polarizers with isotropic media between them) when $\delta=0^0$ and minimum (the sample becomes λ/2 plate) when $\delta=180^0$. It is known that achieving of 180^0 birefringence is required for maximum diffraction efficiency of polarization diffraction gratings. In some of the experiments we put the Wollaston prism and one more photodetector D_2 after the sample, measuring the dichroism by a weak Ar^+ laser beam.

4. RESULTS

First of all, we found that very large birefringence could be induced in our samples under the action of Ar^+ light. Even values higher than $\delta=180^0$ are easily achievable. Following the formula (2) the minimum of curves 1, 2, 3 on fig.3 is the point where the birefringence is 180^0, i.e. the sample becomes almost $\lambda/2$ plate, rotates the polarization azimuth of the probe at 90^0 and it becomes nearly orthogonal to the transmission axes of the polarizer P_3. However, it is not an ideal $\lambda/2$ plate because of the presence of slight dichroism even in the wavelength λ=633 nm. During the excitation, due to birefringence, the polarization after the sample changes from line to expanding ellipse, circle ($\delta=90^0$) and then collapsing ellipse with the long axis turned 90^0 to the initial direction. At $\delta=180^0$ it is again line. Thanks to the nonzero dichroism, this line is not exactly 90^0 rotated to the original, but slightly different. In various experiments we found this value to be usually below 1^0, it is even 0.3^0 for curve 1 on fig. 3. For independent measurements we made a separate setup where the probe beam is linearly polarized under 45^0 to the excitation beam and after the sample we put a Wollaston prism producing 2 linear polarizations respectively parallel and orthogonal to the excitation. The results for He–Ne 633 nm wavelength are compared to that mentioned above. For 488 nm wavelength where the absorbance is much higher we used a weak 1mW Ar^+ laser beam. There is a considerable dichroism there: $D_{ort} - D_{par} = 0.65$, where D_{par} is the optical density for direction parallel to the excitation polarization; D_{ort} is the density for the orthogonal direction. We found (fig. 3, curve3) that for samples excited over the boundary of 180^0 phase delay, after that, during the relaxation, i.e. self-erasure when the pump laser is switched off, the curve can reach lower values than than those during the recording. This means that at that time the dichroism is lower and consequently it erases faster than the birefringence. For curve 3 on fig.3. it is 3.5 times lower (second minimum) than that during the recording (first minimum). We think that this could be due to the faster reorientation, relaxation of the molecules compared to the anisotropically stressed gelatin matrix. This phenomenon is in close connection with the air humidity, i.e. dye molecules mobility and needs further investigation. The gelatin is a medium well known with its water absorbing capability. We found that for longer lasting memory the samples have to be dried for 3 hours in an oven at 60^0C. It can be seen from figure 3, curve 2 that in the baked samples photoanisotropy is induced slower but after the excitation switch off is much more stable in time. This stability depends on the humidity of the laboratory air. In an experiment with blowing hot air to the sample during the recording and after switching off the excitation we obtain that in $T=60^0$C air flow, the relaxation of the sample to isotropic state is quite delayed. As was concluded by Blanche[6], the high glass transition temperature T_g prevents thermal relaxation of trans molecules but does not prevent their reorientation upon polarization light excitation. Thus we think T_g for dry MPY/gelatin samples is above that degree.

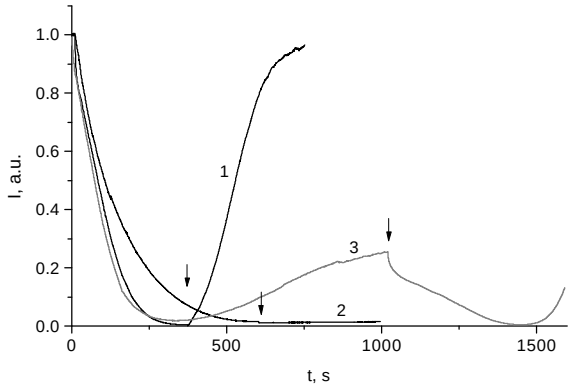

Fig. 3. Recording and selferasure. Arrows point switch off the excitation. (1) – nonbaked sample, (2) – baked sample, (3) excitation for more than 180° anisotropic phase delay

The goal to have a stable memory in our samples is reduced to the problem of how to protect them from air humidity. This is discussed below. At the same time, nonbaked samples can record and erase relatively fast (curve 1, fig.3) i.e. could be used for dynamic memory for multiple cycles record–erase. During the first 2–3 cycles the speed of recording increases until the moving parts of the dye molecules make the surrounding matrix more flexible. Then the consequent cycles in the already formed matrix have a constant speed. If faster erasure is needed, it could be done with circular polarization.

It was difficult to find a material which would adhere firmly to the gelatin layer on the one hand and to be transparent, and to form an isotropic layer with good optical quality on the other hand. Some materials suggested by chemists had not been waterproof enough, other required very high temperature to polymerize. Finally we found that a microscope cover glass plate is appropriate. We stuck it to the sample with an epoxy glue and thus we obtained a recording medium which is 100% protected against the air humidity. We succeeded to record above $\delta=180^0$ birefringence in the so protected sample and found that the

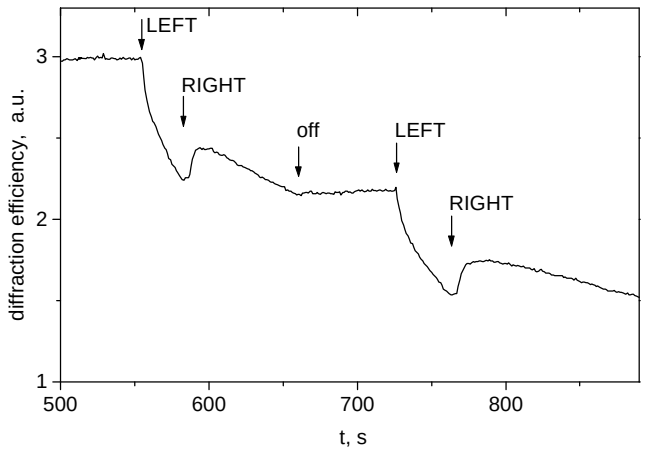

Fig. 4. Erasure of the recorded grating alternatively with left and right circularly polarized beam.

recording is stable for months.

A simple holographic setup was made in order to record polarization gratings. The linearly polarized Ar laser beam first is split in two beams of equal intensity which after passing properly oriented $\lambda/4$ plates become left and right circularly polarized. They interfere onto the sample at an angle of 3.5^0, recording the polarization grating. The read out beam was a circularly polarized He–Ne laser. We achieved a maximum of 67% diffraction efficiency from the input beam, which is 84% from the energy after the sample. In glass protected samples efficiency is stable for months and non-stop radiation of at least 24 hours with the 2mW He–Ne laser was harmless for them.

Acting on the grating with only one of the recording beams, i.e. stopping the other causes erasure. Stopping alternatively the left and the right beam however revealed a very peculiar behaviour – fig.4. The interesting point is that the left circular polarization erases the grating faster while under the action of right circular polarization the diffraction efficiency first increases and after that slowly decreases. To the best of our knowledge similar behavoiur was reported only for azopolymers , where the relief grating takes place[8]. But in our case there is no relief, we checked their surface by means of atomic force microscope. We think this phenomenon needs further investigation.

Scalar gratings recorded with two linear parallel polarizations give a maximum of 3.7% efficiency in the first order. This proves that the reorientation of the polar dye molecules is the main process responsible for the polarization response in this media[9].

In conclusion, a new media (Mordant Pure Yellow azodye in a matrix of gelatin) for polarizarion recording is proposed. High values of induced birefringence in initially isotropic samples are reported ($\Delta n>0.02$, anisotropic phase delay $\delta>180^0$). The recording is sensitive to humidity but could become quasi-permanent by protecting the layer with a cover glass. Polarization holographic diffraction gratings were recorded and a diffraction efficiency of 67% (for 633nm) is achieved. An unusual behaviour is observed when erasing the recording with one of the recording beams. The right circular polarization first causes increase of the efficiency while the left erases ordinarily.

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