## Photoinduced changes in the refractive index of azo-dye/polymer systems

M. Ivanov,<sup>a)</sup> T. Todorov, L. Nikolova, N. Tomova, and V. Dragostinova Central Laboratory of Optical Storage and Processing of Information, Bulgarian Academy of Sciences, Sofia 1113, P. O. Box 95, Bulgaria

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The photoinduced isotropic and anisotropic changes in the refractive index of dye/polymer guest-host systems are investigated. The values obtained are compared to the diffraction efficiencies of scalar and polarization holographic gratings, recorded in the same polymer systems. It is concluded that the induced anisotropy is related to the dye molecules involved in the photoprocesses, whereas the isotropic changes, which are much stronger, are related to the polymer matrix as well. © *1995 American Institute of Physics*.

Nonlinear optical effects in dye/polymer systems offer new possibilities for the production of versatile and highly effective optical and electro-optical devices.<sup>1</sup> Such materials will play an increasingly greater part in telecommunications, optical interconnectors in computers, optical processing, and sensors. A large part of the investigated nonlinear polymer systems involves azo-dyes and light radiation results in trans-cis isomerization, leading to ordering and/or reorientation of their molecules. Thus, optical anisotropy arises (dichroism and birefringence) that can be used for the production of polarization holographic optical elements,<sup>2,3</sup> for polarization-sensitive wavefront phase conjugation,<sup>4,5</sup> etc. Beside birefringence, a very strong isotropic change in the refractive index is observed in some copolymer systems.<sup>6</sup> The influence of the type of dye and matrix on the magnitude of the induced changes and the rate of the processes are studied by many authors in rigid solutions (systems guesthost) and in copolymers.<sup>7–9</sup> Nonetheless, the mechanism of interaction between the polymer matrix and dye in the process of photoinducing the changes in the refractive index is not completely clear.

The present work investigates the isotropic  $(\Delta n_i)$  and anisotropic  $(\Delta n_a)$  changes in the refractive index of rigid solutions of azo-dyes in polymers. A comparison is made between the induced changes in the refractive indices  $\Delta n_i$ and  $\Delta n_a$ , and the diffraction efficiencies of scalar  $(\eta_i)$  and polarization  $(\eta_a)$  diffraction gratings.

The investigated samples are films of rigid solutions of azo-dyes in a polymer matrix. Systems of the bisazo-dye mordant pure yellow (MPY) in poly(vinylalcohol) (PVA) (concentration 5 vol. % and thickness 50  $\mu$ m),<sup>7</sup> and the monoazo-dyes methyl-orange (MO) in poly(vinylalcohol) (0.6 vol. %)<sup>10</sup> and disperse-red19 in polymethylmetacrylate (PMMA) (concentration 0.4 vol. % and thickness 100  $\mu$ m) are used. The layers are prepared by a standard technique—dissolution of the dye and polymer in an appropriate solvent, deposition on a glass substrate, and drying for 24 h at 20 °C and humidity 50%. The concentrations of the dyes are selected in such a way that the optical transmittance of the samples is about 10% for an Ar<sup>+</sup> laser with a wavelength 488 nm, and 80%–90% for a He–Ne laser with a wavelength 633 nm.

The experimental setup includes an Ar<sup>+</sup> laser with  $\lambda$ =488 nm, a He–Ne laser with  $\lambda$ =633 nm, photodetectors, and computer acquisition and processing of the photodetectors signals in real time. The changes in the refractive index  $\Delta n$  are calculated by measuring the reflection coefficient *R* of the samples at  $\lambda$ =488 and 633 nm at an angle of incidence of the measuring light less than 5°. The changes are induced with an Ar<sup>+</sup> laser with a wavelength  $\lambda$ =488 nm.

In order to eliminate the influence of the reflection from the rear plane of the glass substrate, in some of the experiments for measurement of the reflection coefficient R a triangular prism is fastened by immersion to the rear side of the substrates.

Figure 1 shows the change in the reflection from the front surface of a MPY/PVA sample for  $\lambda$ =488 nm. Initially, the inducing light intensity is 20 mW/cm<sup>2</sup>, and in about 60 s it is increased to 600 mW/cm<sup>2</sup>. From the curve it becomes clear that the photostationary value of the change in *R* is reached in about 30 s for both inducing intensities, and that the thirtyfold increase in the intensity results in just an increase of 20%-30% in the reflection coefficient. The photostationary increase in the refractive index, calculated from this experiment, is  $\Delta n$ =0.002. After the inducing beam is turned off, the refractive index diminishes and the reflection coefficient reaches its initial value. The behavior of the curves, reflecting the decrease in the photoinduced change in



FIG. 1. Photoinduced changes in the reflection coefficient *R* of a MPY/PVA sample on irradiation and measurement with an Ar<sup>+</sup> laser ( $\lambda$ =488 nm). The energy density of the irradiating beam is 20 mW/cm<sup>2</sup> during the first 60 s and 600 mW/cm<sup>2</sup> thereafter.

<sup>&</sup>lt;sup>a)</sup>Electronic mail: mivanov@bgearn.bitnet



FIG. 2. Photoinduced change in the reflection coefficient *R* of a MPY/PVA sample on irradiation with an Ar<sup>+</sup> laser beam ( $\lambda$ =488 nm, 450 mW/ cm<sup>2</sup>) and measurement with a wavelength  $\lambda$ =633 nm.

*R* after turnoff of the excitation, depends on the intensity and duration of illumination, as well as on the parameters of the polymer matrix (density, humidity, etc.).

The changes in the reflection coefficient *R* at the same optical excitation, measured at a wavelength  $\lambda$ =633 nm, are considerably greater. Figure 2 illustrates the change in *R* on illumination of the same sample (MPY/PVA) with light with  $\lambda$ =488 nm and *I*=450 mW/cm<sup>2</sup>, the immersion prism being removed. From the rising curve and periodical changes in the reflection coefficient, due to interference of the beams, reflected by the front and rear surface of the samples, we calculated a photoinduced increase in the refractive index of various samples  $\Delta n$ =0.01–0.03.

In the investigations of the other two systems of azodye/polymer-MO/PVA and DR19/PMMA containing monoazo-dye, we found that irradiation with wavelength  $\lambda$ =488 nm had an opposite effect, i.e., the initial refractive index, hence the reflection coefficient, decreased. Figure 3 illustrates the change in *R* on irradiation of a MO/PVA sample with a wavelength  $\lambda$ =488 nm and intensity *I*=450 mW/cm<sup>2</sup>, as in Fig. 2. The changes in the DR19/PVA layers are in the same direction. The sign of photoinduced change in *R* in the different systems is independent of whether the measuring light polarization is parallel or perpendicular to that of the exciting light.

So far, all results concern the change in the isotropic



FIG. 3. Photoinduced change in the reflection coefficient R of a MO/PVA sample. The conditions are as in Fig. 2.

refractive index. As is known, mainly photoinduced anisotropic changes, due to *trans-cis* isomerization,<sup>9,10</sup> are investigated in such systems. In order to investigate the photoinduced birefringence in MPY/PVA samples, we irradiated them with a linearly polarized Ar<sup>+</sup> laser beam and measured the transmittance of the samples through crossed polarizers. At  $\lambda$ =633 nm (outside the absorption band), the induced birefringence in MPY/PVA samples is  $\Delta n_a = n_{\parallel} - n_{\perp} = 5 \times 10^{-4}$ . Here,  $n_{\parallel}$  and  $n_{\perp}$  are the refractive indices of light, polarized parallel and perpendicular, respectively, to the exciting beam polarization.

Holographic gratings were recorded in the same samples, using two plane waves with parallel and orthogonal polarizations. The holographic recording in the second case is due to the polarization sensitivity of the recording material, and the diffraction efficiency depends on the photoinduced anisotropy. The spatial frequency of the recorded gratings was 100 mm<sup>-1</sup>. The diffraction efficiency was measured in real time in the -1 order at  $\lambda$ =488 nm and with a He–Ne laser under Bragg's angle. The diffraction efficiency of the polarization gratings ( $\eta_a$ =0.6%–1%) turned out to be higher than that of scalar gratings ( $\eta_i$ =0.3%–0.4%).

Irradiation with light brings about trans-cis isomerization and reorientation of the molecules of the azo-dyes. Macroscopically, it is observed as a change in the absorption spectrum of the samples and the ensuing change in the refractive index, as well as appearance of dichroism and birefringence. Besides, the motion of molecules or parts of them changes the size and shape of the free spaces around them. This may lead to a change in the matrix density, and hence, in the refractive index of the sample. In Ref. 6, an extremely strong decrease in the refractive index in layers of copolymer PE/DR19 (down to 0.3 at a dye concentration of 68 wt. %) was observed. The authors have shown that this is related to the change in the absorption spectrum of the sample and claim that when the molecules pass from trans into cis form they increase the volume of the free spaces in the matrix, i.e., its density, and hence, its refractive index diminishes. We also observed a decrease in  $n_i$  in the samples in which the polymer matrix is doped with monoazo-dye (MO and DR19).

In samples containing the dye MPY, however, the change in the refractive index is positive, i.e., it increases. The MPY molecules are twice as large as the monoazo-dye molecules; they contain four benzene rings and two double azo bonds around which light can cause spatial rotation. During this isomerization, the molecule is very likely to "contract." Thus, the free spaces in the matrix can become smaller and, therefore, the density of the polymer and the refractive index can increase.

The experiments on recording scalar holographic gratings show that their diffraction efficiency is much smaller than the one expected from the changes in the refractive index  $\Delta n_i = 0.03$ . Such a discrepancy between the measured changes in  $\Delta n_i$  at uniform irradiation and relatively large spatial frequency of the interference fringes (1000 mm<sup>-1</sup>) is also observed in Ref. 6. This can be attributed to the relatively large size of the polymer molecules (5  $\mu$ m) and to spreading of the excitation from the irradiated parts to the nonirradiated ones, i.e., the resolution is limited. For this reason, the great isotropic photoinduced changes in the refractive index in this type of materials can be applied where the requirements to the resolutions are weak, e.g., channel waveguides.

However, the values of the diffraction efficiency of gratings recorded with spatial frequency up to 1000 mm<sup>-1</sup>, using orthogonal polarizations of the two beams, corresponded to the measured values of the photoinduced birefringence. Such correspondence has been observed before both in analogous system "guest-hosts" and in copolymers.<sup>8,9</sup> The presence of this high resolution invokes the conclusion that anisotropic changes in the optical properties of the systems of this kind are due mainly to photoisomerization and to the considerably smaller molecules of the azo-dyes. The changes in the polymer matrix discussed above affect the kinetic parameters of photoanisotropy. The authors are indebted to Dr. Ts. Petrova and Dr. P. Sharlandjiev for helpful advice.

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