*Bulgarian Chemical Communications, Volume 45, Special Issue B (pp. 137-140) 2013*

# Photoinduced anisotropy in azodyes Alizarin Yellow R and Mordant Pure Yellow in a gelatin matrix

D. P. Ilieva[1], L. L. Nedelchev[2*], D. I. Nazarova[2]

[1]*Varna Medical University, Department of medical physics and biophysics,*
*84 Tzar Osvoboditel Blvd., 9000 Varna, Bulgaria*
[2]*Institute of Optical Materials and Technologies – Bulgarian Academy of Sciences,*
*Acad. G. Bonchev Str, bl. 109,1113 Sofia, Bulgaria.*

Received October 17, 2013; Revised November 25, 2013

We present a study of the photoinduced changes in the absorbance spectra D(λ) on illumination with linearly polarized light for two azo dyes – Alizarin Yellow R (AYR) and Mordant Pure Yellow (MPY) in gelatine matrix. The spectra of the photoinduced dichroism ΔD are measured in the UV-visible range. We give an experimental evidence that the cis-form of the bis-azo dye Mordant Pure Yellow is anisotropic and reorients into direction perpendicular to the exciting light polarization. It is also shown that the photoinduced dichroism is stable for one month after the illumination.

Keywords: photoinduced anisotropy, dichroism, birefringence, azo dye, Alizarin Yellow R, Mordant Pure Yellow

## INTRODUCTION

During the last two decades intensive research has been carried out aimed at the development of new media for high-density optical storage. It has been established that azobenzenes are promising for some practical applications in the field of optical data storage, polarization sensitive elements, polarization holography, etc. [1, 2]. Different media based on various organic dyes embedded in a polymeric or gelatine matrix have been studied [3, 4]. The values of the photoinduced birefringence and dichroism are found to strongly depend on the chemical structure of the dye molecule. The holographic recording in photosensitive medium with Weigert effect in the case of linear polarization of the object wave has been investigated theoretically and experimentally [3]. A considerable value of the photoinduced dichroism ($\Delta D = 0.6$ at $\lambda = 488$ nm) of the azo dye Mordant Pure Yellow (MPY) in a matrix of polyvinyl alcohol has been measured [5]. Later MPY in a gelatin matrix has been proposed as a medium for stable polarization recording [6, 7]. Relatively high values of birefringence have been measured (over $\Delta n = 0.02$). High-efficient polarization diffraction gratings were recorded in this material with two circularly polarized waves and their characteristics were investigated [8]. Based on these polarization gratings, a novel type of compact ellipsometric device working with white light was built [9]. Two other types of media for holographic recording are also commonly used – silver halide based materials [10-12], and also photopolymers [13-15].

In this paper we present the results of a spectral investigation of the photoinduced anisotropy in azo dyes Alizarin Yellow R (AYR) and Mordant Pure Yellow (MPY) dispersed in a gelatine matrix.

## EXPERIMENTAL

In these experiments we use two azo dyes: mono-azo dye Alizarin Yellow R and bis-azo dye Mordant Pure Yellow (Fig. 1). The dyes were added to a water solution of gelatin (Rousselot 3552). Their concentration with respect to the gelatin is 2 wt % for AYR and 2.4 wt % for MPY, respectively. Films were made by casting the water solution of gelatin with dyes onto glass plates. The

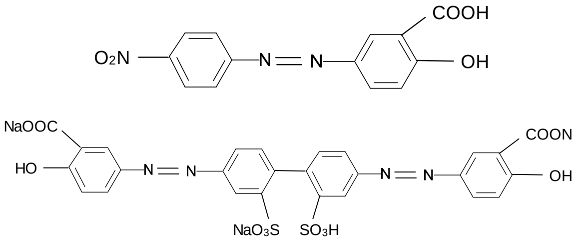

**Fig. 1.** Chemical structures of the azo dyes Alizarin Yellow R (a) and Mordant Pure Yellow (b).

---

* To whom all correspondence should be sent:
E-mail: lian@iomt.bas.bg

films thickness is between 3 and 5 μm. The samples were dried for 24 h at 20 °C and then for another 2 h at 80 °C to remove the residual moisture.

Linearly polarized light from a 200 W mercury lamp was used to induce isomerization of the azo-dyes. The illumination was done directly with the lamp or through filters transmitting 310–460 nm or 370–530 nm respectively. In the case of direct illumination the light intensity was 0.05 mW/cm$^2$. When using the filters, it was 0.03 mW/cm$^2$. The spectral measurements were carried out with a Cary 5E UV–VIS–NIR spectrophotometer (Varian Inc.) in the range 300–550 nm where is the absorbance band of the dyes. From the measured values of transmittance $T$, the absorbance $D$ was easily determined using the Beer-Lambert law: $D = -\log(T)$.

## RESULTS AND DISCUSSION

Curves 1 and 2 on Fig. 2 show the absorbance spectra of the two types of films before the illumination. The absorbance maximum of the Mordant Pure Yellow in gelatin is about 375 nm and for Alizarin Yellow R in gelatin is at 389 nm. After the exposure we measured the absorbance spectra of the samples through a polarizer oriented parallel and perpendicular to the exciting light polarization direction. The corresponding absorbances are denoted as $D_{par}$ and $D_{ort}$ and the dichroism is defined as $\Delta D = D_{ort} - D_{par}$.

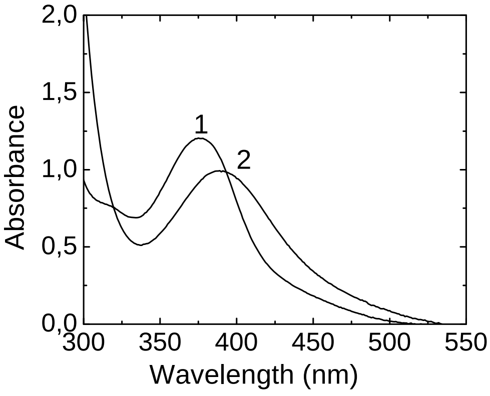

**Fig. 2.** Absorbance spectra of the MPY/gelatin (1) and AYR/gelatin films (2) before illumination.

In Fig. 3 the absorbance spectrum of the Alizarin Yellow R/gelatin film before and after illumination through the filter transmitting light in the range 370–530 nm is shown. $D_o$ is the absorbance before illumination and $D_{ort}$ and $D_{par}$ are the absorbances after 3 h exposure with linearly polarized light with intensity $I = 0.03$ mW/cm$^2$. Similar spectra were measured after exposure directly with mercury lamp and through filter transmitting from 310 nm to 460 nm.

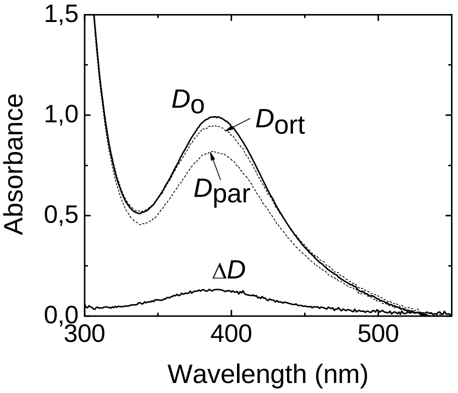

**Fig. 3.** Photoinduced changes in the absorbance of the AYR/gelatin film. $D_o$ –absorbance before the illumination, $D_{ort}$ and $D_{par}$ – polarized absorbance spectra, $\Delta D = D_{ort} - D_{par}$ — dichroism.

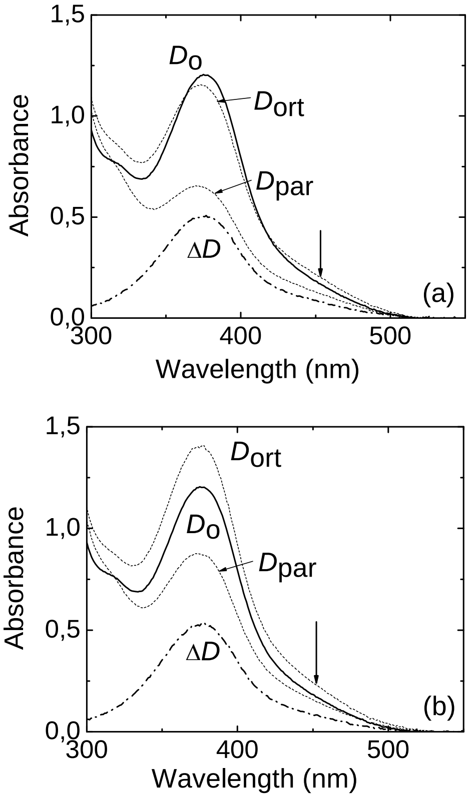

**Fig. 4.** Photoinduced changes in the absorbance of the MPY/gelatin film before and after 2 h exposure, $I = 0.05$ mW/cm$^2$ (a) and measured again after 1 month (b).

In Fig. 4a the absorbance spectra of the bis-azo dye Mordant Pure Yellow in a gelatine matrix before and after 2 hours illumination with linearly polarized light (intensity 0.05 mW/cm$^2$) are presented. Significant changes are seen in the maximum of the absorbance spectrum – anisotropic bleaching mainly of the *trans*-band. On the other hand the absorbance increases at the longer wavelengths (the *cis*-band), as indicated by an arrow on Fig. 4. This is evidence that not only the *trans*- but also the *cis*-isomer of MPY is anisotropic. Our experiments show that photoinduced anisotropy in a Mordan Pure Yellow does not depend on the wavelength of the exciting light. We do not detect considerable changes in the photoinduced dichroism $\Delta D = D_{\mathrm{ort}} - D_{\mathrm{par}}$ in the bis-azo dye during the following one month (Fig. 4b), but we observe an increase of both $D_{\mathrm{ort}}$ and $D_{\mathrm{par}}$, so their average value virtually coincides with $D_{\mathrm{o}}$ before the illumination. We attribute this to a relaxation of the photoinduced bleaching of the azo dye during the illumination.

The maximal photoinduced dichroism of the MPY/gelatin film is higher ($\Delta D = 0.52$) in comparison to the AYR/gelatin film ($\Delta D = 0.13$). This is related with the molecular structure of the azo-dyes. As seen in Fig. 4, the dichroism maximum coincides with the absorbance maximum of the *trans*-molecules.

Along with the dichroism, birefringence was induced in the azo dyes under the action of polarized light from the mercury lamp. We measured the birefringence at 633 nm, outside the absorbance band. Relatively high values of birefringence were obtained for the MPY/gelatin film – $\Delta n = 0.01$. For the AYR/gelatin film $\Delta n$ was 0.001.

It is known that azo dye molecules exist in two isomeric forms: *trans* and *cis*. The *trans*-form is stable in darkness. When illuminating the dye, a process of *trans–cis* isomerization takes place together with a thermal *cis–trans* relaxation. As a result, a photostationary equilibrium is reached in which some of the molecules are in *cis*-form. The inherent absorbance of the *trans*-molecules is highly anisotropic. The absorption of a photon by a *trans*-molecule is proportional to $\alpha_z \cos^2\theta_p$, where $\theta_p$ is the angle between the molecular axis and the electric field (the polarization) of the exciting light. This leads to a selective depletion of the *trans*-molecules parallel to the pump polarization (known also as "angular hole burning" – AHB). The competition between the *trans–cis* optical pumping and *cis-trans* relaxation, results in a stationary angular distribution of *trans*-molecules ($\Omega$ is the solid angle corresponding to the angles $\theta$, $\varphi$):

$$n_T(\Omega) = (N/4\pi)(1 + \Im\cos^2\theta_p)^{-1} \tag{1}$$

where $\Im = I\sigma_T\Phi_{TC}\tau_C$, $I$ is the pump intensity, $\sigma_T$ – the absorption cross section, $\Phi_{TC}$ – the *trans* to *cis* quantum yield and $\tau_C$ is the *cis* lifetime [16]. Hence, the change in the concentration of molecules in the *trans*-form after exposure determines the photoequilibrium *cis*-concentration.

In our case, for the bis-azo dye Mordant Pure Yellow it was established that $D_{\mathrm{ort}}$ at longer wavelengths (corresponding to the *cis*-band) is higher in comparison to $D_0$ (indicated by an arrow on Fig. 4). This is an evidence that the *cis*-molecules are anisotropic. Therefore, we assume that not only the *trans*-, but also the *cis*-isomers are reoriented into direction perpendicular to the exciting light polarization.

## CONCLUSIONS

In summary, we have observed considerable photoinduced changes in the absorbance spectra of Alizarin Yellow R/gelatin film ($\Delta D = 0.13$) and MPY/gelatin film ($\Delta D = 0.52$). We also show that the photoinduced dichroism is stable in time – the curves for $\Delta D$ are virtually the same shortly after the illumination and one month later.

For the first time we experimentally determined that *cis*-form of the Mordant Pure Yellow is also anisotropic. We assume that reorientation of the *cis*-isomers occurs into direction perpendicular to the exciting light polarization.

***Acknowledgement:*** *The authors would like to express their sincere gratitude to Prof. L. Nikolova for the useful discussion and comments.*

## REFERENCES

1. L. Nikolova, P. S. Ramanujam, Polarization Holography, Cambridge Univ. Press, Cambridge, 2009.
2. A. Natansohn, P. Rochon, *Chem. Rev.*, **102**, 4139 (2002).
3. S. S. Petrova, V. G. Shaverdova, *Opt. Spectrosc.*, **101**, 549 (2006).
4. V. Shaverdova, S. Petrova, A. Purtseladze, L. Tarasashvili, N. Obolashvili, *Appl. Opt.*, **48**, 2793 (2009).
5. M. Ivanov, L. Nikolova, T. Todorov, N. Tomova, V. Dragostinova, *Opt. Quant. Electron.*, **26,** 1013 (1994).
6. M. Ivanov, T. Eiju, *Opt. Rev.*, **8,** 315 (2001).
7. M. Ivanov, T. Eiju, *Proc. SPIE*, **4580**, 664 (2001).
8. L. Nedelchev, T. Todorov, L. Nikolova, Tz. Petrova, N. Tomova, V. Dragostinova, *Proc. SPIE*, **4397**, 338 (2001).

9. T. Todorov, L. Nikolova, G. Stoilov, B. Hristov, *Appl Opt*., **46**, 6662 (2007).
10. B. Ivanov, M. Shopova, E. Stoykova, V. Sainov, *Opt. Appl.* 42, 643 (2012).
11. B. Ivanov, E. Stoykova, Ts. Petrova, V. Sainov, *Proc. Bulg. Acad. Sci.*, **64**, 345 (2011).
12. B. Ivanov, M. Shopova, A. Baldjiev, E. Stoykova, V. Sainov, *Proc. SPIE,* **7747**, 77470K (2011).
13. I. Naydenova, S. Martin, V. Toal, *J. Eur. Opt. Soc. Rapid*, **4**, 09042, (2009).
14. K. Pavani, I. Naydenova, S. Martin, R. Howard, V. Toal, *J. Mater. Sci.*, **20**, 198 (2009).
15. K. Pavani, I. Naydenova, S. Martin, V. Toal, *J. Opt. A: Pure Appl. Opt.,* **9**, 43, (2007).
16. M. Dumont, Z. Sekkat, *Proc. SPIE*, **1774**, 188 (1992).

# ФОТОИНДУЦИРАНА АНИЗОТРОПИЯ В АЗОБАГРИЛАТА АЛИЗАРИН ЖЪЛТО Р И ПРОТРАВНО ЧИСТО ЖЪЛТО В МАТРИЦА ОТ ЖЕЛАТИН

*Д. П. Илиева[1], Л. Л. Неделчев[2], Д. И. Назърова[2]*

*[1] Медицински университет “Проф. д-р П. Стоянов”, Катедра по медицинска физика и биофизика,*
*бул. “Цар Освободител” № 84, 9000 Варна, България*
*[2] Институт по Оптически Материали и Технологии, Българска Академия на Науките,*
*ул. Акад. Г. Бончев, бл. 109, 1113 София, България*

Постъпила на 17 октомври 2013 г.; коригирана на 25 ноември, 2013 г.

(Резюме)

В настоящата работа са представени резултатите от изследване на фотоиндуцираните промени в спектрите на поглъщане D(λ) при облъчване с линейно поляризирана светлина за две азобагрила – Ализарин Жълто Р (АЖР) и Протравно Чисто Жълто (ПЧЖ) в матрица от желатин. Спектрите на фотодихроизъм ΔD = Dort – Dpar са измерени в УВ и видимата област. Представено е експериментално доказателство, че цис изомерът на бис-азобагрилото Протравно Чисто Жълто е анизотропен и се преориентира перпендикулярно на посоката на поляризация на въздействащата светлина. Показано е също, че фотоиндуцирания дихроизъм е стабилен един месец след облъчването.