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Pulsed laser induced birefringence switching in a biopolymer matrix containing azo-dye molecules

Jaroslaw Mysliwiec *, Marta Ziemienczuk, Andrzej Miniewicz

Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

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ABSTRACT

All optical switching has been studied using the Optical Kerr Effect (OKE) configuration in a biopolymer matrix containing an azo-dye: the Disperse Orange 3 (DO3). The biopolymer system consisted of a deoxyribonucleic acid blended with cationic surfactant molecule cetyltrimethyl-ammonium chloride is suitable for optical quality thin film fabrication. The excitation beams inducing birefringence were delivered from a continuous wave laser at 532 nm and another nanosecond pulsed Nd: YAG laser. The birefringence was instantaneously monitored under crossed polarizer system by a weak non-absorbed light from a cw He–Ne laser working at 632.8 nm. Fast all optical switching process (in the range of microseconds) and excellent reversibility have been observed.

1. Introduction

In the dynamic holography one needs an optical medium that can be reversibly modified by light in order to make high-resolution hologram. Such materials can then be used in holographic memories or 3D holographic displays [1], for correction of wave-front, object recognition and identification in real time. Typical nonlinear optical materials basing on photophysical mechanisms of refractive index changes, require high optical field intensities for recording (10^7–10^{10} W cm^{-2}) but have very small relaxation times (10^{-8}–10^{-12} s). The necessity of using high power lasers essentially limits wide application of these media. Polarization-sensitive dynamic holographic materials [2–5] are basing on resonant excitation of optically bistable molecules and therefore not require high intensity for hologram inducing light (typically 0.01–10 W cm^{-2}). This together with an inexpensive technology of their production is advantageous for their broad practical application. However, characteristic times of recording/erasing holograms in such materials are of the order of milliseconds [6] stimulating development of materials showing still shorter recording/erasing time constants. This could be done by change of a matrix in which optically bistable molecules perform photoisomerisation steps. Our choice is deoxyribonucleic acid (DNA) which is recognized as not only an important biological material carrying genetic information but also as a useful passive matrix material in the filed of photonics [7]. The disadvantage is that it is soluble only in aqueous solutions. In order to make it processable, i.e. soluble in organic solvents, it is complexed with surfactants. It is clear that the unique chiral structure of DNA and its various forms and complexes (like widely studied DNA–CTMA [8]) result in interesting enough optical and electronic properties that could be exploited in photonic devices [9–13]. Used in this research DNA-based biopolymer was fabricated from the salmon roe DNA by first purifying it and then complexing with a cationic surfactant, cetyltrimethyl-ammonium (CTMA) chloride according to the procedure described by Heckman et al. [9]. To prepare the biopolymeric matrix we used a commercially available purified salmon roe DNA (Sigma–D1626). The complex is well soluble in many organic solvents including alcohols and can be processed into good optical quality thin films either by casting or spin-coating deposition method. This particular matrix incorporating photochromic an azo-dye (Disperse Red 1) turned to be a very promising candidate for fast processing of optical information [14]. In our previous work we reported on fast dynamics (a single millisecond rise and fall times) in optical phase conjugation experiment [15] or optical correlation [16] proving material suitability for real-time holography. Interestingly, the studied systems exhibited an excellent reversibility of the phase conjugate signal generation, with no residual gratings left in the bulk of a material even after few hours of exposure to the partially absorbed laser light. The response speed to light excitation was tentatively explained by an assumption of intercalation [17] or semi-intercalation of a photochromic dye in DNA–CTMA matrix that was confirmed also by Monte Carlo simulations [18].

The purpose of the present research was to investigate the dynamics of all optical switching properties of a modified DNA–CTMA matrix doped with bistable azo-dye molecule Disperse Orange 3 (DO3) (cf. Fig. 1). DO3 has similar structure to Disperse Red 1 but they differ by terminal groups. In this report we study

* Corresponding author.
E-mail address: jaroslaw.mysliwiec@pwr.wroc.pl (J. Mysliwiec).

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optical properties of DO3 molecule for comparison of its functioning in DNA–CTMA matrix.

2. Sample preparation and experimental set-up

We prepared butanol solutions of DNA–CTMA and Disperse Orange 3 separately and mixed them in order to obtain 1% DO3 in DNA–CTMA w/w in the dry mass. The DNA–CTMA: DO3 solution was cast onto microscope glass plates and dried 24 h in air at room temperature. Thickness of the so obtained layers amounted to 3 μm.

An absorbed linearly polarized light is able to introduce molecular alignment into previously random distribution of azo-dye molecules in a polymer matrix. The effect was observed by several research groups but first theoretical explanation of photoinduced alignment mechanisms of azo-dyes in rigid polymeric matrices was elaborated by Dumont et al. [19] and Dumont and Sekkat [20]. The developed mean field model of photoinduced anisotropy assumes multiple photoisomerisation events between *trans* and *cis* isomers of an azo-dye. Three different processes have been considered in this model: angular hole burning (AHB), angular redistribution (AR), and rotational diffusion (RD). A linearly polarized light beam selectively excites molecules whose transition dipole moment axis is near parallel to its polarization plane (probability $\propto \cos^2 \alpha$, where α is the angle between the long axis of the *trans* molecule and the polarization of light). As a part of the excited *trans* molecules may relax to the ground state of the *cis* isomer, which has a relatively long lifetime, optical pumping produces an anisotropic depletion of the angular distribution of the *trans* isomers: this is AHB. During the lifetime of the *cis* state a spontaneous angular rotation (AR) may appear. Because *cis* molecules absorb at the same wavelength, after excitation which can be regarded as polarization independent, they undergo transition to *trans* state at random directions diminishing anisotropy. Rotational diffusion (RD), which is the rotational Brownian motion of *trans* molecules resulting from their thermal agitation, tends to randomize the orientation and then to fill the angular distribution voids [21].

The sum of these effects results in formation of birefringence in an amorphous polymer whose kinetics depends on the light intensity and properties of bistable molecules as well as on their interaction with the nearest environment in the biopolymeric matrix [18].

The photoinduced birefringence and its relaxation were studied using Optical Kerr Effect (OKE). The Optical Kerr Effect is a phenomenon of an optically-induced birefringence in an initially optically isotropic medium. A strong optical field $\bar{E}$ inside a medium causes an asymmetry in the medium's zero-field dielectric tensor due to molecular macroscopic reorientation with long molecular axes aligning perpendicular to the electric field vector of pumping light. The amount of induced birefringence is characterized by the difference between the refractive indices parallel $n_{||}(I)$ and perpendicular $n_{\perp}(I)$ to the optical field (cf. Fig. 2).

For the purpose of the present work we set-up a modified two-beam pulsed-cw OKE experiment which is schematically shown in Fig. 3.

The first excitation (pump) beam is delivered by a cw Nd: YAG laser (doubled in frequency, $\lambda = 532$ nm, 100 mW). The excitation light almost counter propagates through the sample film against a He–Ne laser probe beam of wavelength $\lambda = 632.8$ nm. Detection of the birefringence induced in the sample was obtained via measurement of 632.8 nm light transmittance through the sample positioned in between a crossed polarizer and analyzer system. Detector (Si, Thorlabs) entrance was protected by the glass cut-off filter rejecting 532 nm light. The OKE signals were analyzed with the help of four channel digital Tektronix TDS 220 oscilloscope. Additionally, a Q-switched Nd: YAG laser, supplying pulses of 6 ns duration at a wavelength of 532 nm and 10 Hz repetition rate, was used. A quarter-wave retardation plate placed on the pulsed laser beam allowed generation of different polarization states of pumping light. When a quarter-wave plate is set at 45° with respect to linear polarization of the input laser, the light polarization state is either left or right-circularly polarized.

The linearly polarized probing light (633 nm) incident normally to the sample surface and polarized at angle 45° with respect to the polarization direction of the pump beam will split into two perpendicularly polarized beams traversing the birefringent sample with different phase velocities (cf. Fig. 2). The phase shift $\delta\phi$ between these beams is equal to [22,23]:

$$\delta\phi = \frac{2\pi}{\lambda_0}[n_{||}(I) - n_{\perp}(I)] \cdot d \tag{1}$$

where λ_0 is a vacuum wavelength of the probe field, $n_{||}(I)$ and $n_{\perp}(I)$ are optically induced refractive indices within the film parallel and perpendicular to the pump field polarization, respectively, I is the intensity of the pump beam and d is the film thickness. The pump beam induced changes in refractive indices $\delta n_{||}(I)$ and $-\delta n_{||}(I)$ are small but easily measurable by changes in light intensity of probing beam transmitted by the sample and crossed at 90° with respect to input polarizer a Glan–Thomson polarizer. If analyzer and polarizer transmission axes are mutually orthogonal the incident light intensity I_0 can not be transmitted unless in between polarizers a

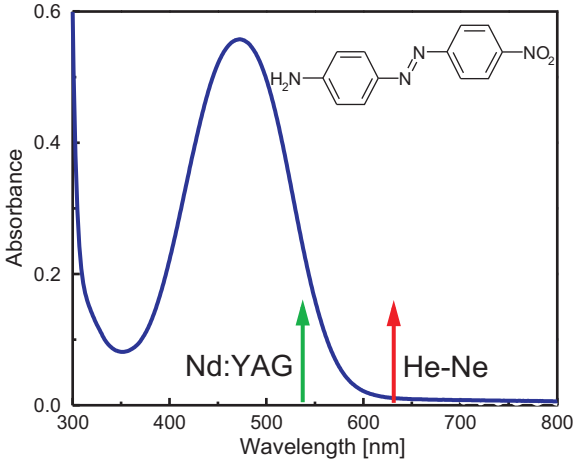

Fig. 1. DNA–CTMA: DO3 film absorption spectrum and chemical structure of Disperse Orange 3 molecule in its elongated *trans* form (inset).

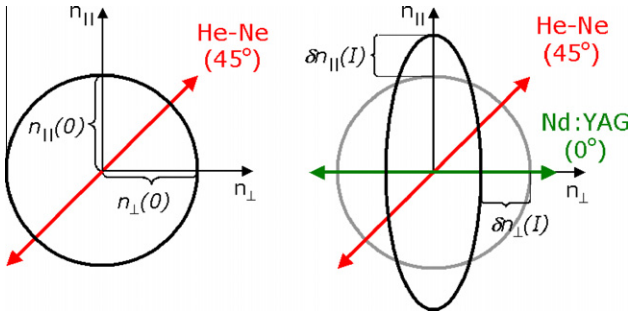

Fig. 2. Scheme of in-plane changes in refractive index of a photochromic layer as a result of pumping with Nd: YAG 532 nm linearly polarized light beam. Left: cross section of refractive index indicatrix for an initially isotropic photochromic biopolymer thin film in the absence of pumping beam $\Delta n = n_{||}\ (I = 0) - n_{\perp}\ (I = 0) = 0$. Right: horizontally polarized pumping beam from Nd: YAG laser induces birefringence $\Delta n = n_{||}(I) - n_{\perp}(I) \neq 0$.