

# Photoreversible optical data recording in films of amorphous azo dye-containing polymers

A.N.Simonov, D.V.Uraev, V.P.Shibaev, S.G.Kostromin

**Abstract.** The photoreversible properties of films of amorphous azo-containing polymers (AAPs) are studied theoretically and experimentally. The control of the sign of a photoinduced addition  $\Delta n^{\text{ind}}$  to the refractive index of the polymer by changing polarisation of the incident light is demonstrated. A theoretical model of photoinduced processes in AAP films is proposed, which takes into account the orientation diffusion of trans-isomers of azo dyes, and simplified analytic approaches describing the photoorientation dynamics in AAPs are considered. The theoretical results are in good agreement with our experimental data.

**Keywords:** azo-containing polymers, optical data recording, polarisation sensitivity.

## 1. Introduction

Photosensitive azo-containing polymers attract great interest as reversible nonlinear-optical media. A high sensitivity and a high spatial resolution, as well as a good stability against repeated exposure to light make these media especially attractive for using in optical data processing, high-density data recording and storage [1–6]. One of the important properties of azo compounds is their polarisation sensitivity, i.e., the dependence of the optical parameters of a medium on the polarisation of the incident light. This property allows the use of azo-containing polymers for the development of optically controlled polarisation-phase transparencies.

Several theoretical models have been proposed to describe the dynamics of photoinduced processes in azo-containing polymer films (see, for example, [4, 5]). In most cases, the authors restricted themselves to the formulation of the problem and a simplified qualitative analysis of the properties of a polarisation-sensitive response of a medium [6]. In this connection the development of the refined theoretical model of photoinduced processes and the

obtaining of analytic solutions of the problem become urgent. The approximation of experimental data by the analytic dependences will give the material parameters of the compound under study.

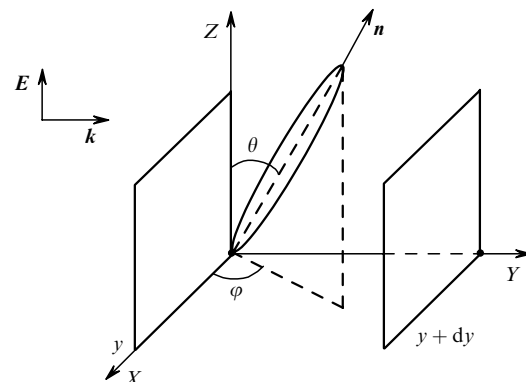
In this paper, we study theoretically and experimentally the optical parameters of films of amorphous azo-containing polymer (AAP). The dynamics of a photoinduced addition  $\Delta n^{\text{ind}}$  to the refractive index of the medium is considered based on the theoretical model for different directions of polarisation of the incident light. The theoretical results are compared with the experimental data obtained.

## 2. Model of photoinduced processes

Consider the interaction of a plane linearly polarised light wave ( $\mathbf{E}$  is the electric-field amplitude,  $\mathbf{k}$  is the wave vector) with a layer of an azo-containing polymer in the configuration shown in Fig. 1. By assuming that the polymer layer  $[y, y + dy]$  is thin, we have  $|\mathbf{E}(y)|^2 = \text{const}$ . Our model of photoinduced processes is based on the assumption that the photosensitivity of an AAP is determined only by *trans*- and *cis*-isomers of the azo dye [3, 7]. We assume, similarly to Ref. [5], that the *trans*-isomer of the dye has a rod-like shape, whereas *cis*-isomers have a spherical symmetry. In this case, the polarisability ( $\hat{\alpha}_{t,c}$ ) and absorption cross section ( $\hat{\sigma}_{t,c}$ ) tensors of *trans*- and *cis*-isomers can be written in the form

$$\hat{\alpha}_t = \text{diag}(0, 0, \alpha_t), \quad \hat{\alpha}_c = \text{diag}(\alpha_c, \alpha_c, \alpha_c),$$

$$\hat{\sigma}_t = \text{diag}(0, 0, \sigma_t), \quad \hat{\sigma}_c = \text{diag}(\sigma_c, \sigma_c, \sigma_c).$$
(1)



**Figure 1.** Configuration of the interaction of an azo dye *trans*-isomer with light in an AAP layer of thickness  $dy$ .

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Hereafter, the subscripts ‘t’ and ‘c’ refer to *trans*- and *cis*-isomers of azo dyes, respectively. The spatial orientation of *trans*- and *cis*-isomers of dyes can be conveniently described by the densities of their angular distributions  $n_t(t, \Omega)$  and  $n_c(t, \Omega)$ , respectively, where  $\Omega$  is the solid angle;  $d\Omega = \sin\theta d\theta d\varphi$ . In this notation, the total concentration of *trans*-isomers is determined by the expression

$$N_t(t) = \int n_t(t, \Omega) d\Omega. \quad (2)$$

The integration in (2) is performed over the entire solid angle  $4\pi$ . Because of the spherical symmetry of *cis*-isomers, the function  $n_c(t, \Omega)$  is independent of the angle  $\Omega$ . Assuming that  $N_0$  is the total concentration of azo dyes, we determine the current concentration of *cis*-isomers

$$N_c = N_0 - \int n_t(t, \Omega) d\Omega. \quad (3)$$

Having absorbed a photon, azo-dye isomers can undergo *trans*  $\leftrightarrow$  *cis* transitions. The conformational rearrangements accompanying these transitions lead to a change in the optical properties of the medium. The rates  $P_{t,c}$  of *trans*- and *cis*-isomerisation are determined by the properties of the medium and the parameters of the incident radiation [8]:

$$P_{t,c} = \frac{\gamma_{t,c}}{\hbar\omega} g \hat{\sigma}_{t,c} : \mathbf{E}\mathbf{E}, \quad (4)$$

where  $\gamma_{t,c}$  is the quantum yield of the *trans*  $\rightarrow$  *cis* and *cis*  $\rightarrow$  *trans* isomerisation;  $g \equiv \bar{n}c_0/4\pi$  is a constant;  $\bar{n}$  is the mean refractive index of the polymer; and  $c_0$  is the speed of light in vacuum. Taking into account expressions (1) in the arrangement shown in Fig. 1, we obtain [9]

$$P_t = \frac{I}{\hbar\omega} \gamma_t \sigma_t \cos^2 \theta \equiv a_t I \cos^2 \theta, \quad (5)$$

$$P_c = \frac{I}{\hbar\omega} \gamma_c \sigma_c \equiv a_c I.$$

Here,  $a_t$  and  $a_c$  are the rates of photoinduced *trans*  $\rightarrow$  *cis* and *cis*  $\rightarrow$  *trans* transitions and  $I = g|\mathbf{E}|^2$  is the incident light intensity.

We will also take into account spontaneous thermal *cis*  $\rightarrow$  *trans* transitions occurring during isomerisation. The thermal relaxation rate is  $P_r = 1/\tau_r$ , where  $\tau_r$  is the lifetime of the *cis*-isomer. Because the difference of energies of the *trans*- and *cis*-states typical for azo dyes is  $\Delta E \gg k_B T$  (for  $T \sim 300$  K), the probability of the reverse spontaneous *trans*  $\rightarrow$  *cis* transition is very low [6].

The angular reorientation of azo dyes plays an important role along with photoisomerisation. The orientation of the *trans*-isomer can be changed during the repeated events of *trans*  $\leftrightarrow$  *cis* photoisomerisation, as well as due to the rotational diffusion [10, 11]. The rate of diffusion processes is determined by the mobility of isomers and depends on a number of parameters: the molecular environment (packing density), the length of spacers, the temperature of a medium, etc. [4, 12]. In the absence of irradiation by light, diffusion results in the isotropic distribution of azo chromophores, and upon irradiation the diffusion prevents a complete photoinduced reorientation of *trans*-isomers.

Taking expressions (3) and (5) into account, we can write the rate equation for the distribution function of *trans*-isomers of the azo dye in the form

$$\begin{aligned} \frac{\partial n_t}{\partial t} = & -a_t I n_t \cos^2 \theta + \frac{1}{4\pi} \left( \frac{1}{\tau_r} + a_c I \right) \\ & \times \left( N_0 - \int n_t d\Omega' \right) + D \Delta_\Omega n_t. \end{aligned} \quad (6)$$

Here, the diffusion contribution is taken into account phenomenologically;  $D = k_B T/\zeta$  is the rotational diffusion coefficient;  $\zeta$  is the orientation viscosity, which depends on the type of the molecular environment and temperature [4, 10];  $\Delta_\Omega$  is the Laplacian acting on the angular variables  $\theta$  and  $\varphi$ .

The first term in the right-hand side of equation (6) describes a decrease in the amount of *trans*-isomers, which are oriented at an angle of  $\theta$  with respect to the light-wave vector  $\mathbf{E}$ , due to a direct *trans*  $\rightarrow$  *cis* photoisomerisation. The second term describes an increase in the concentration of *trans*-isomers caused by the reverse *cis*  $\rightarrow$  *trans* transition and thermal relaxation. The factor  $1/4\pi$  corresponds to the absence of the orientation memory of dyes [5, 13]. Let us supplement equation (6) with the initial condition of the type  $n_0 = n_t(t=0, \theta) = N_0/4\pi$ , assuming that before irradiation by light the AAP contained only isotropically distributed *trans*-isomers.

Equation (6) can be applied to a thin AAP layer when  $I(y) = \text{const}$ . For a polymer layer of an arbitrary thickness, absorption of light propagating in the medium should be taken into account:

$$\begin{aligned} \frac{dI(y, t)}{dy} = & -\beta I(y, t) \equiv - \left\{ \sigma_t \int n_t(y, t, \Omega) \cos^2 \theta d\Omega \right. \\ & \left. + \sigma_c \left[ N_0 - \int n_t(y, t, \Omega) d\Omega \right] \right\} I(y, t). \end{aligned} \quad (7)$$

The nonlinear absorption coefficient  $\beta$  consists of two components corresponding to contributions from *trans*-isomers and spherically symmetric *cis*-isomers. As a boundary condition, we will specify the intensity  $I(y=0, t) = I_0$  at the entrance to the AAP. By solving simultaneously equations (6) and (7), we can find the expressions for isomer concentrations  $n_t(y, t, \theta)$  and  $n_c(y, t, \theta)$  in different layers  $y$  of the polymer sample ( $0 \leq y \leq L$ , where  $L$  is the AAP film thickness).

By using the found distribution function  $n_t(t, \theta)$ , we can calculate the photoinduced change in the dielectric constant in a thin AAP layer [9] for the light polarised parallel to the vector  $\mathbf{E}$ :

$$\begin{aligned} \Delta \varepsilon_{\parallel}^{\text{ind}}(t) & \equiv \varepsilon_{\parallel}(t) - \varepsilon_{\parallel}(t=0) \\ & = 4\pi\alpha_t \left[ \int n_t(t, \Omega) \cos^2 \theta d\Omega - \int n_t(t=0, \Omega) \cos^2 \theta d\Omega \right] \\ & + 4\pi\alpha_c \left[ N_0 - \int n_t(t, \Omega) d\Omega \right]. \end{aligned} \quad (8)$$

The photoinduced addition  $\Delta \varepsilon_{\parallel}^{\text{ind}}$  is caused by the changes in the concentration and the angular distribution of *trans*-

isomers (the first term), as well as by the appearance of *cis*-isomers (the second term). Taking into account that  $\Delta\varepsilon_{\parallel}^{\text{ind}}/\bar{\varepsilon} \ll 1$  ( $\bar{\varepsilon} = \bar{n}^2$  is the dielectric constant of the unperturbed medium), we obtain the photoinduced addition to the refractive index  $n$

$$\Delta n_{\parallel}^{\text{ind}}(t) = \frac{1}{2\bar{n}} \Delta\varepsilon_{\parallel}^{\text{ind}}(t). \quad (9)$$

For the light polarised perpendicular to the vector  $\mathbf{E}$ , the addition  $\Delta\varepsilon_{\perp}^{\text{ind}}(t)$  can be determined similarly

$$\begin{aligned} \Delta\varepsilon_{\perp}^{\text{ind}}(t) &\equiv \varepsilon_{\perp}(t) - \varepsilon_{\perp}(t=0) \\ &= 4\pi\alpha_t \left[ \int n_t(t, \Omega) \sin^2 \theta \cos^2 \varphi \, d\Omega \right. \\ &\quad \left. - \int n_t(t=0, \Omega) \sin^2 \theta \cos^2 \varphi \, d\Omega \right] + 4\pi\alpha_c \left[ N_0 - \int n_t(t, \Omega) \, d\Omega \right]. \end{aligned} \quad (10)$$

### 3. Analytic solution

Because an exact analytic solution of the integro-differential equation (6) cannot be obtained, we will use some simplifying approximations. We will analyse equation (6) for a thin AAP layer by two different methods, which are based on the expansion of the required solution  $n_t(t, \theta)$  into a power series in  $t$  [9] or in Legendre polynomials [4, 6, 10].

To derive the solution that is valid for short times  $t \ll \tau_0$ , where  $\tau_0 = \min\{\tau_d, \tau_r, (a_t I)^{-1}, (a_c I)^{-1}\}$  and  $\tau_d^{-1}$  is the characteristic diffusion time, it is convenient to represent  $n_t(t, \theta)$  as a power series in  $t$ . Let us assume that  $D = 0$  in equation (6). Assuming that the relative change in the concentration of *trans*-isomers is small, we represent  $n_t(t, \Omega)$  in the form

$$n_t \approx n_t^{(0)} + n_t^{(1)} + n_t^{(2)} + \dots, \quad (11)$$

where  $n_t^{(k)} \sim t^k$ . By substituting (11) into equation (6) and equating the terms of the same order of smallness, we obtain a system of coupled equations. The substitution  $n_t(t, \theta) = n_t^{(0)} + n_t^{(1)}$  gives the equation for the first correction  $n_t^{(1)}$

$$\begin{aligned} \frac{\partial n_t^{(1)}}{\partial t} &= -a_t I \cos^2 \theta n_t^{(0)} \\ &\quad + \frac{1}{4\pi} \left( \frac{1}{\tau_r} + a_c I \right) \left( N_0 - \int n_t^{(0)} \, d\Omega' \right). \end{aligned} \quad (12)$$

Here, according to the initial conditions,  $n_t^{(0)} = n_t(t=0, \theta) = N_0/4\pi$ .

By restricting ourselves to the first correction in a series (11), we can obtain the expression for  $n_t^{(2)}(t, \theta)$ . Finally, the concentration  $n_t(t, \theta)$ , with an accuracy to terms  $\sim (t/\tau_0)^2$ , takes the form

$$n_t(t, \theta) = \frac{N_0}{4\pi} \left[ 1 - A(\cos^2 \theta)t + \frac{1}{2}A^2(\cos^4 \theta)t^2 + Bt^2 \right], \quad (13)$$

where  $A = a_t I$  and  $B = a_t I(a_c I + 1/\tau_r)/6$ .

By substituting the concentration  $n_t(t, \theta)$  (13) of *trans*-isomers into (8)–(10), we obtain the following expressions for photoinduced additions to the refractive index

$$\begin{aligned} \Delta n_{\parallel}^{\text{ind}}(t) &= \frac{2\pi}{\bar{n}} N_0 \left[ \left( \frac{1}{3} \alpha_c - \frac{1}{5} \alpha_t \right) At \right. \\ &\quad \left. - \frac{1}{2} \left( \frac{1}{5} \alpha_c - \frac{1}{7} \alpha_t \right) A^2 t^2 - \left( \alpha_c - \frac{1}{3} \alpha_t \right) Bt^2 \right], \end{aligned} \quad (14)$$

$$\begin{aligned} \Delta n_{\perp}^{\text{ind}}(t) &= \frac{2\pi}{\bar{n}} N_0 \left[ \frac{1}{3} \left( \alpha_c - \frac{1}{5} \alpha_t \right) At \right. \\ &\quad \left. - \frac{1}{10} \left( \alpha_c - \frac{1}{7} \alpha_t \right) A^2 t^2 - \left( \alpha_c - \frac{1}{3} \alpha_t \right) Bt^2 \right]. \end{aligned}$$

The expressions for photoinduced additions  $\Delta\beta_{\parallel}^{\text{ind}}$  and  $\Delta\beta_{\perp}^{\text{ind}}$  to the absorption coefficients have a similar form.

The accuracy of the solution obtained above can be improved by substituting the series  $n_t(t, \theta)$  with a greater number of terms into the initial equation (6). However, for  $t > \tau_d$ , the role of rotational diffusion becomes significant, and the above solution is invalid in this time interval. Let us use in this case another approximation, which allows us to describe the effect of diffusion processes and to obtain the solution of equation (6) for any instant of time  $t$ .

Taking into account the diffusion term, we will seek a solution as a series in Legendre polynomials  $n_t(t, \theta) = \sum_i T_i(t) P_i(\cos \theta)$ . Assuming the series rapidly converging, we will restrict ourselves to a finite number of expansion terms. By equating the factors at the Legendre polynomials of the same order, we obtain from equation (6) a system of differential equations for expansion coefficients  $T_i(t)$ . Because of the distribution function is symmetric [ $n_t(t, \theta) = n_t(t, \pi - \theta)$ ], all the coefficients  $T_i(t)$  of the odd order vanish. The numerical analysis of equation (6) shows that we can restrict ourselves, with a sufficient accuracy, to three terms of the expansion of  $n_t(t, \theta)$  in the Legendre polynomials, second-order terms inclusive [4], i.e., we can seek the solution of (6) in the form

$$n_t(t, \theta) = T_0(t) + T_2(t) P_2(\cos \theta). \quad (15)$$

By substituting (15) into (6), we obtain the equations for expansion coefficients

$$\begin{aligned} \frac{\partial T_0}{\partial t} &= - \left( \frac{1}{3} a_t I + a_c I + \frac{1}{\tau_p} \right) T_0 \\ &\quad - \frac{2}{15} a_t I T_2 + \frac{1}{4\pi} \left( a_c I + \frac{1}{\tau_r} \right) N_0, \\ \frac{\partial T_2}{\partial t} &= - \frac{2}{3} a_t I T_0 - \left( \frac{11}{21} a_t I + 6D \right) T_2. \end{aligned} \quad (16)$$

The system (16) can be solved for the coefficients  $T_0(t)$  and  $T_2(t)$ . By substituting the series (15) with the found coefficients into expressions (8)–(10), we obtain the required expressions for photoinduced additions to the refractive index in the AAP layer:

$$\begin{aligned} \Delta n_{\parallel}^{\text{ind}}(t) &= \frac{8\pi^2}{\bar{n}} \left\{ \left[ n_0 - T_0^s - \tilde{T}_1 \exp\left(-\frac{t}{\tau_1}\right) \right. \right. \\ &\quad \left. \left. - \tilde{T}_2 \exp\left(-\frac{t}{\tau_2}\right) \right] \left( \alpha_c - \frac{1}{3} \alpha_t \right) + \frac{2}{15} \alpha_t \left[ T_2^s - C(\lambda_1) \tilde{T}_1 \times \right. \right. \end{aligned}$$

$$\begin{aligned} & \times \exp\left(-\frac{t}{\tau_1}\right) - C(\lambda_2)\tilde{T}_2 \exp\left(-\frac{t}{\tau_2}\right) \Bigg\}, \\ \Delta n_{\perp}^{\text{ind}}(t) = & \frac{8\pi^2}{\bar{n}} \left\{ \left[ n_0 - T_0^s - \tilde{T}_1 \exp\left(-\frac{t}{\tau_1}\right) \right. \right. \\ & \left. \left. - \tilde{T}_2 \exp\left(-\frac{t}{\tau_2}\right) \right] \left( \alpha_c - \frac{1}{3} \alpha_t \right) - \frac{1}{15} \alpha_t \left[ T_2^s - C(\lambda_1)\tilde{T}_1 \right. \right. \\ & \left. \left. \times \exp\left(-\frac{t}{\tau_1}\right) - C(\lambda_2)\tilde{T}_2 \exp\left(-\frac{t}{\tau_2}\right) \right] \right\}, \end{aligned} \quad (17)$$

where  $\tau_1$  and  $\tau_2$  are the characteristic times of collective rearrangements in the medium;  $T_i^s$  are coefficients characterising the distribution function  $n_i(t, \Omega)$  upon saturation;  $T_i^s = T_i(t \rightarrow \infty)$ ;  $\tilde{T}_i$  are the amplitudes of the variation in the distribution function ( $T_0^s + \tilde{T}_1 + \tilde{T}_2 = n_0$ );  $C(\lambda_1)$  and  $C(\lambda_2)$  are constants; and  $\lambda_{1,2} = 1/\tau_{1,2}$ . The explicit expressions for coefficients  $T$ ,  $C$ , and  $\tau$  are not presented because they are cumbersome.

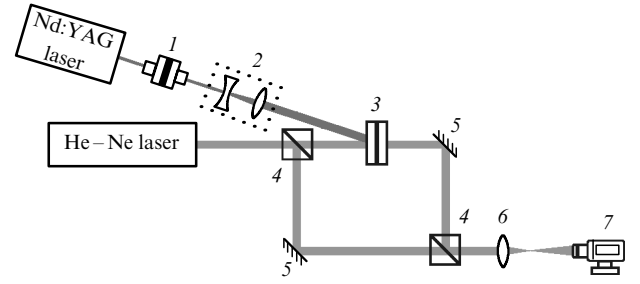
By expanding  $n_i(t, \theta)$  into a series in the Legendre polynomials (15), we restricted ourselves to the second-order terms inclusive. This restricts the temporal region  $t$  of applicability of the solutions obtained. Analysis of initial equation (6) near saturation, when  $\Delta n(t) \sim \Delta n_s^{\text{ind}}$  (where  $\Delta n_s^{\text{ind}}$  is the photoinduced addition to the refractive index upon saturation), shows that the solutions obtained above are invalid.

#### 4. Experimental

The results presented in this paper were obtained for films of a ridge-like Polymer-11 polymethyl methacrylate copolymer containing oxycyano-azo-benzene fragments with a molecular concentration of 60% in the side chains of the macromolecule [12]. Polymer films with the working aperture area of  $\sim 4 \text{ cm}^2$  and the thickness  $L \approx 15$  and  $50 \text{ }\mu\text{m}$  were placed between glass substrates. One of the substrates contained a conducting transparent  $\text{SnO}_2$  layer (for heating the substrate) and was equipped with a thermal sensor. Samples were heated and their temperature was stabilised during experiments using an electronic thermal control system.

The polymer under study has good holographic properties [14]. For example, the diffraction efficiency of  $50\text{-}\mu\text{m}$  thick AAP films was  $\sim 80\%$  at the spatial frequency  $\sim 2000 \text{ mm}^{-1}$  and the holographic sensitivity achieved  $1 \text{ cm}^2 \text{ J}^{-1}$ . The maximum spatial resolution of an AAP can exceed  $6000 \text{ mm}^{-1}$  [1].

Fig. 2 shows the scheme of the experimental setup for measuring the dynamics of a photoinduced addition to the refractive index  $\Delta n^{\text{ind}}(t)$  for different polarisations of the incident light. The setup consists of a Mach–Zehnder interferometer, with a cell with a sample placed in one of its arms. Samples were irradiated by a frequency-doubled cw LTN402A Nd:YAG laser at  $532 \text{ nm}$ . The laser emission wavelength falls into the wing of the absorption band of azo dyes, providing the efficient excitation of the medium. The operating wavelength of the interferometer (emission of a He–Ne laser at  $\lambda_{\text{pr}} = 633 \text{ nm}$ ) lies outside the absorption band of the polymer and has no effect on it. The probe and pump radiations were linearly polarised. The polarisation plane of the pump radiation was rotated with the help of an electrooptical modulator.

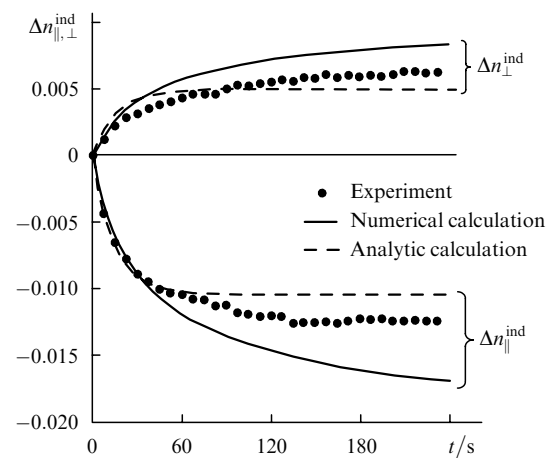


**Figure 2.** Scheme of the experimental setup for measuring  $\Delta n^{\text{ind}}(t)$ : (1) electrooptical modulator; (2) telescope; (3) cell with an AAP film; (4) beamsplitter; (5) mirror; (6) objective; (7) CCD camera.

We recorded in experiments the displacement of interference fringes caused by the local variations in the refractive index of the polymer film induced by laser radiation. The dynamics of displacement of the interference fringes gives information on the change in the refractive index  $\Delta n^{\text{ind}}(t)$  of the medium. The algorithm for processing interference patterns was based on the correlation analysis of the images obtained using a special software package. The error of measurements of  $\Delta n^{\text{ind}}$  was  $\sim 10^{-4}$ .

#### 5. Discussion of results

The experimental dependences  $\Delta n^{\text{ind}}(t)$  for parallel and orthogonal polarisations of the probe and pump light are shown by dots in Fig. 3. The measurements were performed for  $I \approx 210 \text{ mW cm}^{-2}$  and at  $50^\circ\text{C}$ . One can see that the sign of the photoinduced addition  $\Delta n^{\text{ind}}$  to the refractive index is determined by the polarisation of the pump radiation. In the case of parallel polarisations of the probe and pump waves, the refractive index of the AAP decreases ( $\Delta n_{\parallel}^{\text{ind}} < 0$ ), while for orthogonal polarisations of these waves, the refractive index increases ( $\Delta n_{\perp}^{\text{ind}} > 0$ ). Within the framework of the above theoretical model of photoinduced processes in AAPs, such behaviour can be explained as follows. During repeated *trans*  $\leftrightarrow$  *cis* transitions, dyes oriented along the direction of polarisation of the pump



**Figure 3.** Dynamics of  $\Delta n_{\parallel, \perp}^{\text{ind}}(t)$  in a Polymer-11 AAP film of thickness  $L = 50 \text{ }\mu\text{m}$  for parallel and orthogonal polarisations of the pump and probe beams for  $I \approx 210 \text{ mW cm}^{-2}$  ( $\lambda = 532 \text{ nm}$ ) at  $50^\circ\text{C}$ .

light (along the vector  $E$ ) are predominantly ‘burnt out’ from the angular distribution of *trans*-isomers. Due to the reverse *cis*  $\rightarrow$  *trans* photoisomerisation, *trans*-isomers are distributed isotropically over angles. This reduces the concentration of *trans*-isomers oriented along the vector  $E$ , thereby reducing their contribution to the refractive index of the medium ( $\Delta n_{\parallel}^{\text{ind}} < 0$ ). Simultaneously, the number of *trans*-isomers oriented perpendicular to the vector  $E$  increases, so that  $\Delta n_{\perp}^{\text{ind}} > 0$ .

The appearance of anisotropy of the angular distribution of azo dye isomers in the initially isotropic medium is equivalent to the appearance of an optical axis. The photoinduced birefringence  $\delta n^{\text{ind}} = n_{\parallel}^{\text{ind}} - n_{\perp}^{\text{ind}}$  is determined by the properties of an AAP and the parameters of the incident light (its wavelength and exposition).

The optical nonlinearity of the AAP can be explained by the appearance of *cis*-isomers and the angular reorientation of *trans*-isomers of the dye. The anisotropy of optical properties of the polymer is caused by the anisotropic distribution of *trans*-isomers. Spherically symmetric *cis*-isomers make no contribution to the anisotropy of optical properties of the AAP. In the general case the optical properties of a medium substantially depend on the type of the dominating mechanism of optical nonlinearity [15, 16].

When the rate of *trans*  $\leftrightarrow$  *cis* photoisomerisation is negligible compared to the diffusion rate ( $\tau_d \ll (a_t I)^{-1}$ ,  $(a_c I)^{-1}$ ), the photoinduced anisotropy is completely suppressed by thermal diffusion. This results in the isotropic angular distribution of azo dye isomers, and photoinduced additions  $\Delta n^{\text{ind}}$  and  $\Delta \beta^{\text{ind}}$  are independent of the polarisation of a probe wave. In the opposite case, when  $\tau_d \gg (a_t I)^{-1}$ ,  $(a_c I)^{-1}$ , the medium has no time to ‘relax’ to the isotropic distribution and an optical axis appears.

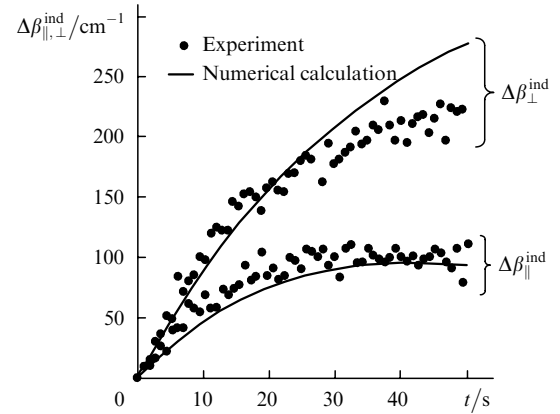
The dashed curves in Fig. 3 show the results of the analytic calculation of the dynamics of  $\Delta n_{\parallel,\perp}^{\text{ind}}(t)$  performed using expressions (17). According to the experimental conditions,  $I \approx 210 \text{ mW cm}^{-2}$  ( $\lambda = 532 \text{ nm}$ ). We used the following parameters of the AAP in the calculations:  $N_0 \approx 1.2 \times 10^{21} \text{ cm}^{-3}$ ,  $\gamma_t = \gamma_c \approx 0.1$  [9],  $\tau_i = 100 \text{ s}$  [6],  $\sigma_t \approx 2.8 \times 10^{-18} \text{ cm}^2$ ,  $\sigma_c \approx 3.1 \times 10^{-18} \text{ cm}^2$ ,  $\alpha_t \approx 1.5 \times 10^{-23} \text{ CGSE units}$ ,  $\alpha_c \approx 4.5 \times 10^{-24} \text{ CGSE units}$ . The values of  $\alpha_{t,c}$  and  $\sigma_{t,c}$  were determined by approximating the experimental data by analytic dependences (14) obtained in the approximation of small  $t$ .

We imposed the restrictions on the possible shape of the angular distribution of *trans*-isomers in deriving the analytic solution (17). By using the series (15), we neglect the contribution from high-order expansion terms, assuming that the anisotropy of the distribution function  $n_i(t, \theta)$  is small. At the initial stage of the exposure, the optical nonlinearity is mainly determined by spherically symmetric *cis*-isomers. In this case, the anisotropy of  $n_i(t, \theta)$  is very small, and the analytic curve coincides with the experimental data. At long exposures, the role of orientation process increases, resulting in the deviation of the theoretical dependence from the experiment, i.e., the expansion (15) is no longer valid.

Because the initial equation (6) is complicated, we performed numerical calculations, using the third-order Runge–Kutta method. To simplify calculations, we assumed that  $D = 0$ , i.e., we considered the dynamics of  $n_i(t, \theta)$  by neglecting diffusion processes. Such a situation takes place at low temperatures  $T < T_g$  (where  $T_g$  is the glass transition temperature) [14]. In the case  $D \neq 0$ , the found solution is valid for  $t \ll \tau_d$ .

The solid curve in Fig. 3 represents the numerical solution of equation (6). One can see from the curves in Fig. 3 that the branch  $\Delta n_{\parallel}^{\text{ind}}(t)$  is located below the experimental curve, whereas the branch  $\Delta n_{\perp}^{\text{ind}}(t)$  is located above the experimental curve. This is explained by the approximation chosen. By setting  $D = 0$ , we excluded the effect of disordering processes that reduce the anisotropy of distribution of *trans*-isomers. The consideration of diffusion results in a decrease in the induced optical anisotropy of the medium, thereby reducing the absolute values of  $\Delta n_{\parallel}^{\text{ind}}(t)$  and  $\Delta n_{\perp}^{\text{ind}}(t)$  (these branches being approached to each other).

Similar reasoning is also valid for the dynamics of variation in the absorption coefficient of the medium shown in Fig. 4. The numerical analysis shows that under the experimental conditions chosen, the diffusion coefficient  $D \sim 10^{-3} \text{ rad}^2 \text{ s}^{-1}$ . For this value of  $D$ , the experimental and theoretical dependences virtually coincide.



**Figure 4.** Dynamics of  $\Delta \beta_{\parallel,\perp}^{\text{ind}}(t)$  in a Polymer-11 AAP film of thickness  $L = 15 \mu\text{m}$  for parallel and orthogonal polarisations of the pump and probe beams for  $I \approx 25 \text{ mW cm}^{-2}$  ( $\lambda = 532 \text{ nm}$ ) at  $50^\circ\text{C}$ .

Note that the optical properties of AAP films are independent of the prehistory of the temperature regime. The polymer temperature determines the dynamics of relaxation processes [14]. For  $T < T_g$ , the relaxation of the induced refractive index is negligible, providing a long-term (for several years) storage of holograms.

## 6. Conclusions

We have studied theoretically and experimentally photoinduced processes in AAP films and have found experimentally the dependence of the sign of the photoinduced addition  $\Delta n^{\text{ind}}(t)$  to the refractive index on the polarisation of the incident light. We have proposed a simplified model of the mechanisms of optical data recording in amorphous azo compounds. Based on the model proposed, the analytic expression has been obtained for the dynamics of variation  $\Delta n^{\text{ind}}(t)$  in the refractive index and the material parameters of the medium have been determined. The optical parameters of the AAP have been calculated more accurately numerically. The results of the theoretical study are in good agreement with the experimental data.

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