

Analytical Description of the Effect of Laser Radiation on Optical Properties of Amorphous Azo-Containing Polymers

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Abstract—The mechanism of the effect of linearly polarized cw laser radiation on optical characteristics of amorphous azo-containing polymers is studied. An effective approach to reducing a phenomenological model of light-induced processes that occur in such a polymer is proposed. This approach allows one to obtain the analytical dependences of the refractive index and absorption coefficient of the polymer on the intensity of the radiation it is exposed to and the exposure time. The theoretical results are compared with experimental data obtained by interferometric measurements of light-induced changes, Δn , in the refractive index of the polymer. The two phenomenological coefficients contained in the model are extracted from experimental dependences of Δn on time. As a result, the model yields analytical results that agree well with the experimental data.

One of the important achievements of organic chemistry, widely used in modern laser physics, is the development of methods for synthesizing photosensitive azo-containing polymers, both amorphous and liquid-crystalline [1]. Such media can be effectively used, for example, in holography and information storage systems [2]. A distinctive feature of the azo-containing polymers is a long response time, which is about a few minutes at room temperature. Heating the material to about 70°C allows one to decrease the response time to fractions of a second [3]. This makes it possible to use an azo-containing polymer as a dynamic nonlinear medium, for example, in pattern-formation experiments with systems of the “Kerr slice with a feedback mirror” type. This idea seems to be promising in the sense of looking for new spatiotemporal regimes to develop in such systems. The expectation is based on the fact that the optical nonlinearity of the considered polymers is more complex than the Kerr nonlinearity: laser radiation locally changes not only the refractive index of the irradiated polymer but its absorption coefficient as well. At the same time, no analytical description of these light-induced processes, which could be incorporated into a general model of an optical feedback system based on an azo-containing polymer film, has been suggested so far.

In this Letter, we propose an effective approach to reducing a phenomenological model of light-induced processes that occur in such a polymer. This approach allows one to obtain the analytical dependences of the optical properties of the polymer on its temperature, the intensity of the radiation it is exposed to, and the exposure time. The theoretical results are compared with

experimental data obtained by interferometric measurements of light-induced changes in the refractive index of the polymer.

In an azo-containing polymer, azo-chromophores can exist either in *cis*- or *trans*- state, the latter corresponding to lower binding energy (the *trans*- and *cis*-isomers have absorption peaks at wavelengths of 360 and 470 nm, respectively [4], so the difference between their activation energies is about 70 kJ/mole). Therefore, in the absence of light irradiation, almost all the chromophores are in the *trans* state, even if the polymer is heated up to a temperature of about 100°C. Linearly polarized cw laser radiation induces *trans-cis* isomerization of those chromophores absorbing incident photons. The *trans*-isomers show strong anisotropy of absorption cross-section. The cross-section depends on the angle θ between the long axis of the isomer and the polarization direction of the laser radiation as $\cos^2\theta$ [5]. Absorption anisotropy of the *cis*-isomers is much weaker [6]. In our model, we shall consider them fully isotropic. This considerably simplifies the theory while causing no significant errors, because, as it will be shown below, the light-induced changes in the optical properties of an azo-containing polymer is primarily due to reorientation of *trans*-isomers. At the same time, the photo-stationary concentration of *cis*-isomers remains low even if the intensity of the incident radiation is high. This is because there are two mechanisms of *cis-trans* isomerization, light-induced and thermal. All these physical processes are taken into account in the following phenomenological equation for the orientation distribution function of the *trans*-isomers, $n(\theta, t)$, which is structurally analogous to the equation sug-

gested by Pedersen *et al.* [5] for liquid-crystalline azobenzene polymers:

$$\begin{aligned} & \frac{\partial n(\theta, t)}{\partial t} \\ = & \frac{\alpha}{2} \left(1 - \int_0^\pi n(\theta, t) \sin \theta d\theta \right) - \beta n(\theta, t) \cos^2 \theta \quad (1) \\ & + \gamma \left(\frac{1}{2} - n(\theta, t) \right), \end{aligned}$$

where t is time, α and β are the rate coefficients of light-induced *cis-trans* and *trans-cis* isomerization, respectively, and γ is the rate of thermal relaxation of the orientation distribution function of the *trans*-isomers to the steady state $n \equiv \frac{1}{2}$ (in the absence of irradiation).

The expression enclosed in the first parentheses is the fraction of *cis*-isomers among all the azo-chromophores contained in the polymer. Equation (1) has two essential differences from Pedersen's model. First, as it has been already pointed out, our model does not take into account the weak anisotropy of the *cis*-isomers. Second, we suppose that a sequence of conformational changes that occur in the course of *cis-trans* and *trans-cis* isomerization causes a chromophore to rotate by an arbitrary angle [7]. The rate coefficients α and β are proportional to the intensity of the incident radiation, while their ratio is a constant determined by the absorption cross-sections of the *cis*- and *trans*-isomers and by the quantum efficiencies of the reactions of light-induced *cis-trans* and *trans-cis* isomerization. For the azo-chromophores considered, this ratio indirectly measured by Simonov amounts to $r_R \equiv \alpha/\beta \approx 1.8$ [8]. Thus, it is possible to rewrite Eq. (1) as

$$\begin{aligned} \frac{\partial n(\theta, t)}{\partial t} = & \frac{r_R \beta(I)}{2} \left(1 - \int_0^\pi n(\theta, t) \sin \theta d\theta \right) \quad (2) \\ & - \beta(I) n(\theta, t) \cos^2 \theta + \gamma \left(\frac{1}{2} - n(\theta, t) \right), \end{aligned}$$

where I is the intensity of the incident radiation. Equation (2) contains two phenomenological parameters: the proportionality factor in the dependence of β on I and the rate of thermal relaxation γ that depends on the polymer temperature.

Such integro-differential equations are usually solved by expanding the function $n(\theta, t)$ into a series (the basis can be, for example, Legendre polynomials). This approach causes either low accuracy of calculations [9] or a large number of equations in the reduced system [5]. The novelty and efficiency of the approach proposed here lie in the fact that we are not interested in the $n(\theta, t)$ function itself. Instead of that, we are going to track the evolution of two moments of this function, which determine such optical properties of

the polymer as refractive index and absorption coefficient, namely: $N(t) \equiv \int_0^\pi n(\theta, t) \sin \theta d\theta$ and $p(t) \equiv \int_0^\pi n(\theta, t) \cos^2 \theta \sin \theta d\theta \equiv \langle \cos^2 \theta \rangle$. The first moment is the fraction of *trans*-isomers among all the azo-chromophores contained in the polymer, while the second characterizes the anisotropy of the orientation distribution of the *trans*-isomers (the completely isotropic distribution corresponds to $p = 1/3$). It can be easily shown that the light-induced change in the refractive index of the polymer for the incident radiation depends on the moments N and p as follows [8]:

$$\Delta n = \kappa \left[p - \frac{1}{3} + r_p(1 - N) \right], \quad (3)$$

where the coefficient κ is proportional to the polarizability of the *trans*-isomers and to the overall concentration of azo-chromophores in the polymer, and r_p is the ratio of the polarizabilities of the *cis*- and *trans*-isomers. A similar expression can be written for the light-induced change in the absorption coefficient of the polymer.

By integrating over θ (taking into account the Jacobian $\sin \theta$) both Eq. (2) and the same equation multiplied by $\cos^2 \theta$, it is possible to obtain the following system of ordinary differential equations for the moments N and p :

$$\frac{dN}{dt} = (\gamma + \beta r_R)(1 - N) - \beta p, \quad (4)$$

$$\frac{dp}{dt} = \frac{1}{3}(\gamma + \beta r_R) - \frac{1}{3}\beta r_R N - \gamma p - \beta \langle \cos^4 \theta \rangle_{n(\theta, t)}.$$

The main difficulty of further analyzing Eq. (4) is the necessity of taking into account the fourth-order moment. This could be evidently done by increasing the number of equations in ODE system (4) and introducing moments of higher even orders up to the moment whose value could be considered negligible. However, this would lead to quite cumbersome expressions for the sought parameters. Therefore, we have chosen another approach based on analyzing the dependence of $\langle \cos^4 \theta \rangle_{n(\theta, t)}$ on p , revealed by numerical computations [2]. It has been found that for a wide range of the rate coefficients β and γ this dependence can be fitted by a liner function:

$$\langle \cos^4 \theta \rangle_{n(\theta, t)} \approx \frac{3}{4}p - \frac{1}{20}. \quad (5)$$

A considerable difference (>30%) between the fitting function (5) and the actual dependence is observed only for strongly anisotropic distributions of *trans*-isomer orientation ($p < 0.1$), which are formed at high intensities of the laser radiation incident on the polymer ($\beta \gg \gamma$).

Equation (4) supplemented with substitution (5) evidently has an analytical solution. Since it is rather cumbersome, we restrict ourselves to writing down the

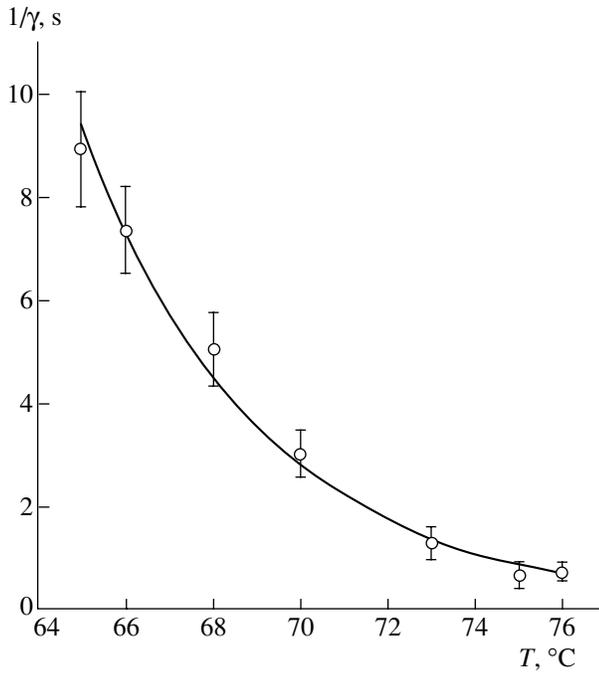


Fig. 1. Relaxation time of the light-induced anisotropy of *trans*-isomer orientation versus the polymer temperature. Experimental data are fitted by an exponential function.

expressions for the steady-state values of the moments, \bar{N} and \bar{p} :

$$\bar{N} = \frac{(5r_R - 3/5)\beta^2 + (5 + 12r_R)\gamma\beta + 12\gamma^2}{5r_R\beta^2 + (12r_R + 9)\gamma\beta + 12\gamma^2}, \quad (6)$$

$$\bar{p} = \frac{3/5r_R\beta^2 + (3/5 + 4r_R)\gamma\beta + 4\gamma^2}{5r_R\beta^2 + (12r_R + 9)\gamma\beta + 12\gamma^2}.$$

The analysis of the first of these expressions shows, in particular, that at $r_R = 1.8$ the fraction of *cis*-isomers (e.g., $1 - N$) does not exceed 0.1 no matter how high is the intensity of the radiation incident on the polymer. It is also easy to show that the fixed point (\bar{N}, \bar{p}) is unconditionally stable. This follows from the analysis of the solutions of the characteristic equation of Eq. (4), which are the following:

$$\lambda_{1,2} = -\gamma - \beta \left[\frac{3}{8} + \frac{r_R}{2} \pm \frac{1}{24} \sqrt{144r_R^2 - 24r_R + 81} \right]. \quad (7)$$

By substituting Eq. (6) into Eq. (3), it is possible to obtain an analytical dependence of the steady-state value of Δn on the phenomenological coefficients β and γ . This dependence was compared with experimental results.

In experiments, we used a 15 μm -thick film of a side-chain polymethacrylic polymer containing 10 mol % of oxycyanoazobenzene fragments in side chains of macromolecules, which had been synthesized at the Chemistry Department of Moscow State Univer-

sity by the group of Prof. Shibaev. The film was placed in an optical cell comprising a heater. A digital temperature control unit was capable of stabilizing the polymer temperature in the range from 30 to 100°C with a maximum deviation of 0.1°C. The cell was inserted into the object arm of a Mach-Zehnder interferometer, where a fringe pattern with a characteristic period of about 0.1 mm was produced by a He-Ne laser beam ($\lambda_1 = 633$ nm, $P = 1$ mW) expanded to a diameter of 5 mm. The light-induced processes were locally excited in the film by the beam of a Nd:YAG laser with intracavity frequency doubling ($\lambda_2 = 532$ nm, $P_{\text{max}} = 100$ mW). The absorption cross-section of the azochromophores at 633 nm is much smaller than at 532 nm. Therefore, the intense green beam served as a pump, while the low-intensity red beam served as a probe. Both beams were linearly polarized in the vertical plane. The measurement technique involved imaging an interferogram with a CCD camera, transferring the image to a personal computer, and calculating the fringe shift caused by the pump beam (with sub-pixel accuracy). Evidently, the light-induced change in the refractive index of the polymer can be calculated using the formula $\Delta n = \delta\lambda_1/d$, where δ is the fringe shift divided by the fringe period and $d = 15$ μm is the thickness of the polymer film.

The aim of the first experiment was to determine how the rate of thermal relaxation γ depends on the polymer temperature. For each temperature value (all ranging from 65 to 76°C), the pump beam first irradiated the polymer for about 20 s and then was blocked. Thus, we recorded the process of relaxation of the light-induced anisotropy of the orientation distribution of the *trans*-isomers (with a step of 0.09 s). The dependence $\Delta n(t)$ was fitted by an exponent, whose characteristic decay time is an estimate of the value $1/\gamma$ (it follows from Eq. (7) that in the absence of the pump radiation, that is, for $\beta = 0$, $\lambda_{1,2} = -\gamma$). The results of these measurements are shown in Fig. 1. The experimental points

are fitted by an empirical formula, $A \exp\left(-\frac{B}{T - T_0}\right)$, where T is the polymer temperature, and T_0 , A and B are fitting parameters [10].

The goal of the next experiment was to determine the rate constant β by analyzing the characteristic stabilization time of Δn under the action of the pump radiation. It follows from Eq. (7) that this process is two-exponential, and numerical calculations show that the accuracy of determining the "slower" time (τ_2) on the basis of the curve $\Delta n(t)$ is much higher than that for the "faster" time (τ_1). Therefore, the value of β was determined from the equation $\tau_2 = -1/\lambda_2$. The experiments showed that the dependence of β on the pump radiation intensity could be expressed as β [s^{-1}] = $(9 \pm 1)I$ [W/cm^2].

After both rate coefficients of the model had been determined, it became possible to compare the experimental and theoretical results on the basis of the steady-state values of Δn at different intensities of the pump radiation. The corresponding dependences are shown

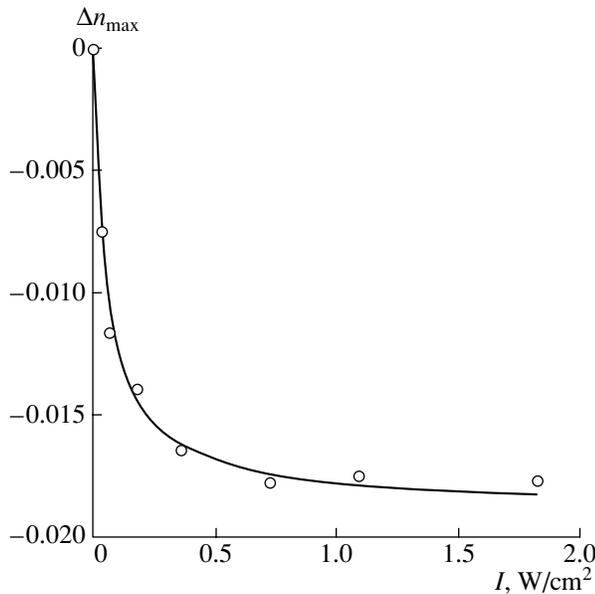


Fig. 2. Maximum light-induced change in the refractive index of the polymer versus the pump radiation intensity: experimental data (dots) and the theoretical dependence based on Eqs. (3) and (6) (solid curve). The polymer temperature is 68°C.

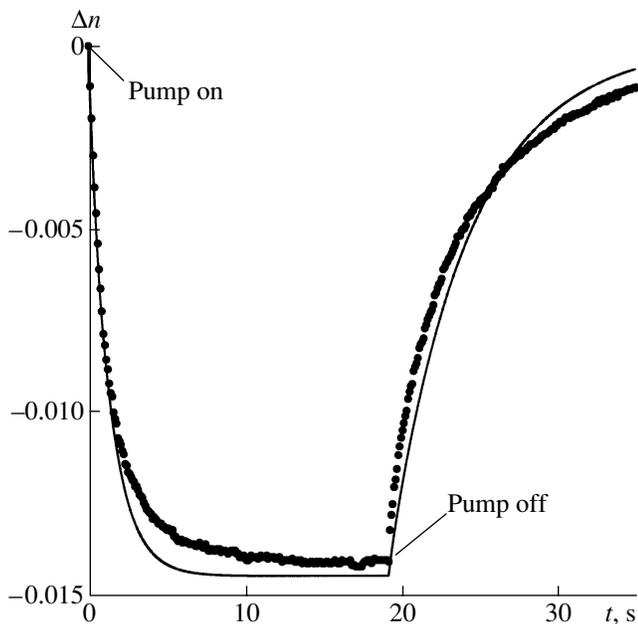


Fig. 3. Typical evolution of the light-induced change in the refractive index of the polymer: experimental data (dots) and the analytical solution of Eq. (4) with approximation (5) (solid curve). The arrows mark the moments when the pump radiation is switched on and off. The polymer temperature is 68°C; the pump radiation intensity is 180 mW/cm².

in Fig. 2. The theoretical plot is based on Eqs. (3) and (6), where the isomer polarizability ratio is set as 0.33 [9] and the scaling factor κ is a fitting parameter. As it can be seen from Fig. 2, the suggested theory quite accurately describes the saturation process of Δn_{\max} ,

despite the fact that the rate coefficients β and γ were determined from the relaxation curves with no use of the dependence $\Delta n_{\max}(I)$. Typical relaxation curves (both experimental and theoretical) are shown in Fig. 3. Their discrepancy observed at the stage of formation of the light-induced Δn is due to the fact that the scaling factor κ was determined from the dependence $\Delta n_{\max}(I)$, that is, so as to satisfactorily describe all the relaxation curves recorded. The discrepancy between the experimental and the theoretical curve after the pump beam is switched off is due to the fact that the relaxation process is actually multi-exponential [7, 11]. The reason of this is different mobility of different azo-chromophores, associated with a nonuniform distribution of free volume in the polymer. Therefore, the rate coefficient γ can be treated as an effective parameter that characterizes the average reorientation time of the *trans*-isomers.

Thus, the proposed approach adequately explains the light-induced processes that occur in an amorphous azo-containing polymer and allows one to obtain the analytical dependences of the optical properties of the polymer on the exposure time and pump radiation intensity, as well as on the polymer temperature (through the $\gamma(T)$ dependence measured experimentally). These dependences seem to be simple enough to be incorporated into a mathematical model of an optical feedback system based on an azo-containing polymer film.

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