

# Model of optically induced memory in amorphous azopolymers

Yu.V. Ponomarev, S.A. Ivanov

**Abstract.** A phenomenological model of the light–azopolymer radiation interaction is proposed in which chromophores interact with the polymer matrix due to the mutual orientational diffusion. It is established that for some amorphous azopolymers, the model satisfactorily describes the photoinduced dichroism dynamics both at the stage of light action and relaxation, and allows the estimate of the main optical parameters of chromophores (absorption cross section and quantum yields of trans and cis isomerisations, times of the spontaneous decay of cis isomers) to be obtained by the experimentally measured dichroism. The comparison of the results of model calculations with the experimental ones shows that only a part of trans isomers participating in trans–cis isomerisation contributes to the dichroism.

**Keywords:** azo dye, induced optical anisotropy, dichroism.

## 1. Introduction

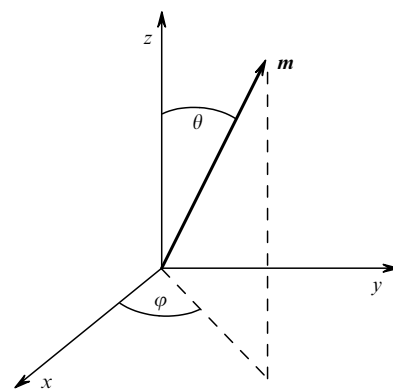
The phenomenological theory of the light–azopolymer interaction was proposed by Sekkat and Dumont [1, 2] and then developed by Sekkat [3, 4]. Although the theory adequately described the dynamics of the processes in the azopolymer at the initial stage of irradiation [5], it could not provide the ‘optical memory’ phenomenon because it took into account only the free orientational diffusion of chromophores. The attempts to allow, at the phenomenological level, for the influence of the polymer matrix and thus to explain the optical memory phenomenon were made in a number of papers. In papers [6–9], the anisotropy of the polymer matrix–chromophore interaction was accounted for within the framework of the mean field theory. The authors of papers [10, 11] took into account the influence of the polymer matrix by using the kinetic approach. Note that the results obtained with the help of the above approaches were compared with the experimental results only at the stage when the polymer was irradiated and the relaxation process, which leads to the appearance of the optical memory effect, was not considered.

In this paper we propose a model taking into account the

anisotropy of the chromophore–polymer matrix interaction within the framework of the mutual orientational diffusion model, which, for a number of amorphous azopolymers, allows one to describe satisfactorily the dynamics of the photoinduced dichroism both at the stage of irradiation and relaxation.

## 2. Photoorientation model in azopolymers with account for optical memory

Consider the dynamics of trans–cis isomerisation in a thin azopolymer layer under the action of light linearly polarised along the  $z$  axis at the frequency  $\omega$  and the intensity  $I$ , propagating along the  $y$  axis perpendicular to the output face of the sample. We assume that in the initial state all the chromophores are the trans isomers with the rod-like shape [12, 13] and their spatial orientation is described by the unit vector  $\mathbf{m}(\Omega) = \{\cos \varphi \sin \theta, \sin \varphi \sin \theta, \cos \theta\}$  (Fig. 1). In this approximation, the optical absorption of trans isomers in the coordinate system bound with a chromophore molecule is described by the tensor  $\hat{\sigma}_t$  with the only nonzero component  $\sigma_t$ . We will assume that the trans-isomer molecules are optically isotropic [14] and characterised by the absorption cross section  $\sigma_c$ . We will describe the distribution of the cis-isomer molecules over the angles  $\Omega$  with the help of the function  $n_t(\Omega, t)$  [ $N_t(t) = \int n_t(\Omega, t) d\Omega$  is the concentration of trans isomers]. The action of light leads to trans–cis and cis–trans isomerisations with the velocities  $a_t I \cos^2 \theta$  and  $a_c I$ , where  $\theta$  is the angle between the trans-isomer axis and the light field



**Figure 1.** Geometry of interaction of the azopolymer trans isomer with radiation.

Yu.V. Ponomarev, S.A. Ivanov Department of Physics, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119992 Moscow; e-mail: ponomarev.yu@mail.ru

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vector;  $a_{c,t} = \gamma_{c,t} \sigma_{c,t} (\hbar\omega)^{-1}$ ;  $\gamma_{c,t}$  is the quantum yield of cis–trans and trans–cis isomerisations. Due to the isotropy of the optical properties of the cis isomers, their distribution over the angles  $\Omega$  is isotropic and the concentration  $N_c(t)$  can be written in the form

$$N_c(t) = N_0 - \int n_t(\Omega, t) d\Omega, \quad (1)$$

where  $N_0 = N_c(t) + N_t(t)$  is the concentration of the chromophore molecules.

The amorphous azopolymers studied in this paper consist of the main polymer chain and side groups or fragments [15, 16]. The side fragments (mesogens) are attached to the main chain with the help of ‘flexible spacers’. The linear dimensions of these fragments with a rod-like shape are equal to  $\sim 15 - 20 \text{ \AA}$  and are significantly smaller than the dimensions of the main chain (100  $\text{\AA}$  and larger depending on the polymerisation degree) [15]. In the case of homopolymers, the side fragments consist of azo dye molecules. In the case of copolymers, the azo dye molecules enter only into a part of the side fragments [16, 17]. At a temperature lower than the glass transition temperature, the translational motions in the system are virtually frozen over; however, the orientational motions are preserved both in the side fragments and in the main chain. We will take into account only the orientational interactions of the chromophores and polymer matrix fragments including the main polymer chain and will neglect the orientational interaction of polymer chains with each other. We will describe phenomenologically the azo dye–polymer matrix interaction by introducing the angular distribution function  $f(\Omega, t)$  [ $\int f(\Omega, t) d\Omega = (4\pi)^{-1}$ ], which characterises the angular anisotropy of the matrix [10].

We will consider first the chromophore–matrix interaction in the absence of light and cis isomers by assuming that their lifetime is comparably small. Let the angular distributions of trans isomers and matrix fragments be isotropic [ $N_c = 0$ ,  $n_t(\Omega)/N_0 = f(\Omega) = (4\pi)^{-1}$ ] and equilibrium in the initial state (an annealed sample). We will introduce weak anisotropy in the angular distribution of the trans isomers, for example, with the help of a short exposure to linearly polarised radiation. The angular distribution of the system consisting of chromophores and polymer matrix fragments will become nonequilibrium. The interaction of the chromophore with the matrix will result in a change in the angular position of both the chromophore ( $\delta\Omega_t$ ) and the matrix fragment ( $\delta\Omega_m$ ) interacting with it; in this case,  $\langle \delta\Omega_t^2 \rangle \gg \langle \delta\Omega_m^2 \rangle$ . Due to these random interaction acts, the angular distribution of both the chromophores and matrix fragments will change. In this case, in the quasi-equilibrium state the angular distributions of the chromophores and the matrix will be the same and different from the isotropic. We will assume that the rates of changes of  $N_0^{-1} \partial n_t / \partial t$  and  $\partial f / \partial t$  during the transition to the quasi-equilibrium state are proportional to the difference  $n_t(\Omega)/N_0 - f(\Omega)$  and are different for  $n_t$  and  $f$ . We will represent the described process (in the first approximation) as mutual orientational diffusion of the chromophore molecules and the polymer matrix fragments with the diffusion coefficients  $D_1$  and  $D_2$ , respectively ( $D_1 \gg D_2$ ).

If we take into account the orientational interaction of the polymer chains with each other and their orientational mobility, which is significantly smaller than the orientational

mobility of the chromophores, the model under study should be supplemented with the ‘intrinsic’ orientational diffusion of the polymer chain with the coefficient  $D_M \ll D_1, D_2$ ; after this, the isotropic distribution of all the components will become equilibrium. Therefore, the time of the optical memory ‘existence’ is determined by the orientational interaction of the polymer chains and can take the values from several hours to years [15, 16]. Below, we will neglect the orientational mobility of the polymer chains, which is caused by their interaction.

The absorption of light by an azopolymer, apart from photoisomerisation, is accompanied also by the local heating both of the light-absorbing chromophore molecule and of its closest surrounding [3, 4]. This can lead to the fact that the diffusion coefficients  $D_1, D_2, D_M$  will differ at the stages of irradiation and relaxation. The experiments showed that at room temperature, these differences would be insignificant for the samples under consideration.

Taking into account the above approximations, the system of equations describing the dynamics of the angular anisotropy of the trans isomers and polymer matrix can be written in the form

$$\begin{aligned} \frac{\partial n_t(\Omega, t)}{\partial t} = & -a_t I \cos^2 \theta n_t(\Omega, t) + \frac{1}{4\pi} \left( a_c I + \frac{1}{\tau_c} \right) \\ & \times \left[ N_0 - \int n_t(\Omega, t) d\Omega \right] \\ & + D_1 \Delta_\Omega \left[ n_t(\Omega, t) - f(\Omega, t) \int n_t(\Omega, t) d\Omega \right], \end{aligned} \quad (2a)$$

$$\frac{\partial f(\Omega, t)}{\partial t} = D_2 \Delta_\Omega \left[ f(\Omega, t) - n_t(\Omega, t) \int n_t(\Omega, t) d\Omega \right], \quad (2b)$$

where  $\Delta_\Omega$  is a Laplacian. The first term in equation (2a) describes a decrease in the trans isomers caused by the trans–cis isomerisation due to the light action. The second term reflects the change in the angular distribution of trans isomers caused by cis–trans isomerisation and spontaneous decay of cis isomers, which is described by the cis-isomer lifetime  $\tau_c$ . The coefficient  $(4\pi)^{-1}$  appeared due to the fact that we neglected the orientational memory in the trans–cis–trans isomerisation process [4]. The last term reflects the influence of the polymer matrix anisotropy on the angular distribution anisotropy of the trans isomers. Equation (2b) describes the dynamics of the angular distribution anisotropy of the polymer matrix fragments, the anisotropy ‘transfer’ from the trans isomers to the polymer matrix being faster than the inverse process ( $D_1 > D_2$ ). The form of the diffusion terms in the equations is caused by the normalisation of the functions  $n_t(\Omega, t)$  and  $f(\Omega, t)$ . It follows from equations (2) that after terminating the irradiation ( $I = 0$ ) and spontaneous decay of cis isomers, the stationary distribution  $f(\Omega) = n_t(\Omega)/N_0$  is established, which differs from the isotropic and reflects the optical memory induced in the polymer matrix. Note that this stationary state depends both on the intensity and the light action duration.

If in the initial state (before irradiation) the polymer matrix and, hence, trans isomers were in the isotropic state, the solution of the system of equations (2) can be searched for in the form of the series expansion in Legendre polynomials. In this case, due to the symmetry of the

functions  $n_t(\theta, t) = n_t(\pi - \theta, t)$  and  $f(\theta, t) = f(\pi - \theta, t)$ , only even-order terms

$$n_t(\Omega, t) = \frac{1}{4\pi} N_0 \sum_{j=0}^{\infty} T_{2j}(t) P_{2j}(\cos \theta), \quad (3)$$

$$f(\Omega, t) = \frac{1}{4\pi} \sum_{j=0}^{\infty} F_{2j}(t) P_{2j}(\cos \theta)$$

will be present in the expansion. The system of equations for the expansion coefficients will have the form

$$\begin{aligned} \frac{dT_0}{dt} &= -a_t I \left[ \left( \frac{1}{3} + A \right) T_0 + \frac{2}{15} T_2 - A \right], \\ \frac{dT_n}{dt} &= -a_t I [A_{n-2}^{(n)} T_{n-2} + A_n^{(n)} T_n + A_{n+2}^{(n)} T_{n+2}] \\ &\quad - D_1 n(n+1)(T_n - T_0 F_n), \\ \frac{dF_n}{dt} &= -D_2 \left( F_n - \frac{T_n}{T_0} \right), \end{aligned} \quad (4)$$

where  $n$  is the positive even number;

$$\begin{aligned} A &= \frac{a_c}{a_t} + \frac{1}{\tau_c a_t I}; \quad A_{n-2}^{(n)} = \frac{n(n-1)}{(2n-3)(2n-1)}; \\ A_n^{(n)} &= \frac{(n+1)^2}{(2n+3)(2n+1)} + \frac{n^2}{(2n+1)(2n-1)}; \\ A_{n+2}^{(n)} &= \frac{(n+1)(n+2)}{(2n+5)(2n+3)}. \end{aligned}$$

The initial conditions for the coefficients of system (4) have the form  $T_0(0) = 1$  and  $T_n(0) = F_n(0) = 0$ . Note that the most important for the induced anisotropy are the coefficients  $T_0$ ,  $T_2$ , and  $F_2$ . The coefficient  $T_0(t)$  is the relative trans-isomer concentration,  $F_0 = 1$  due to the normalisation, and the coefficients  $T_{2j}(t)$  and  $F_{2j}(t)$  ( $j \geq 1$ ) reflect the angular distribution anisotropy of the trans isomers and polymer matrix fragments.

The system of equations (4) has a stationary solution, which is achieved during infinitely long irradiation. The stationary values are independent of the diffusion coefficient  $D_1$  and  $D_2$  and are determined only by the parameter  $A$ . By neglecting the contribution of the coefficients  $T_n$  at  $n > 6$ , we obtain

$$T_0^{\text{st}} \approx \frac{1}{1 + 0.1/A}, \quad T_2^{\text{st}} \approx -1.9T_0. \quad (5)$$

It follows from system (4) that the dependences  $T_0(t)$  and  $T_2(t)$  differ significantly. The time dependence of the coefficient  $T_2$  reflecting the angular distribution anisotropy of the trans isomers can be divided into two stages. The switching on of incident radiation due to the trans-cis and cis-trans isomerisations results in the reorientation of the trans isomers leading to the anisotropy of their angular distribution, which causes an increase in  $|T_2(t)|$ . At the second stage, there become significant the diffusion processes of the angular distribution anisotropy transfer from the trans isomers to the matrix and back, which proceed at different rates determined by the diffusion coefficients. The stationary state in which  $F_2^{\text{st}}(t) = T_2^{\text{st}}(t)$  is achieved during

the time  $t_{\text{st}} \propto \max(D_1^{-1}, D_2^{-1})$ . If the light action is switched off before the stationary state is achieved, a transfer to a new stationary state occurs due to relaxation, the angular distribution anisotropy being stored both in the trans isomers and in the matrix. Note that at the stage of the azopolymer irradiation, the anisotropy changes monotonically with increasing the irradiation dose.

The time dependence of the coefficient  $T_0$  also consists of two stages. At the first stage, trans isomerisation results in the appearance of cis isomers, the concentration of the trans isomers decreases and achieves a minimal value  $T_0^{\text{min}} \propto (1 + 0.3/A)^{-1}$  determined by the competition between the cis-trans and trans-cis isomerisations and by the spontaneous decay of the trans isomers during the time of the order  $[a_t I (1/3 + A)]^{-1} \ll \max(D_1^{-1}, D_2^{-1})$ . At the second stage, the influence of the increase in the angular distribution anisotropy of the trans isomers is manifested, which leads to a monotonic increase in the concentration of the trans isomers up to the stationary value.

We considered above an azopolymer sample with a low optical density  $K_0 = \beta_0 d \ll 1$ , where  $\beta_0$  and  $d$  are the absorption coefficient and its thickness. Because the wavelength of radiation affecting the azopolymer is usually selected in the spectral region of the trans-isomer absorption ( $n-\pi^*$  transition), then, as a rule, the optical thickness of the sample proves greater than unity. The account for the optical density leads to the fact that according to the Bouguer law the radiation intensity decreases as it propagates inside the sample:  $I(y) = I_0 \exp(-\int_0^y \beta(y) dy)$  [ $\beta(y)$  is the absorption coefficient taking into account its light-induced change], the rates of the trans-cis and cis-trans isomerisation processes also decreasing with depth. To take into account the optical density, the sample was divided into  $M$  thin layers inside which the intensity was assumed constant. For each layer, we solved system (4) with the intensity calculated by the Bouguer law by neglecting the light-induced change in the absorption coefficient [ $\beta(y) = \beta_0$ ]. In this case, we calculated the layer-averaged expansion coefficients

$$\bar{T}_n(t) = \frac{1}{M} \sum_{i=1}^M T_n^{(i)}(t), \quad \bar{F}_n(t) = \frac{1}{M} \sum_{i=1}^M F_n^{(i)}(t).$$

The allowance for the optical thickness of the sample leads to two basic effects: an increase in the time required to achieve the stationary state and a decrease in the stationary value of the angular distribution anisotropy of the trans isomers [5].

The optically induced dichroism and birefringence are the brightest manifestations of the optical activity of the azopolymers. In the initial state, when the cis isomers are absent and the trans isomers are distributed isotropically, the optical density of the sample is  $K_0 = \frac{1}{3} \sigma_t N_0 d$ . Under the action of light linearly polarised along the  $z$  axis, trans-cis-trans isomerisation results in the change in the trans-isomer orientation. The change in the optical density for the probe radiation with the same wavelength and polarisation parallel ( $\Delta K_y$ ) and perpendicular ( $\Delta K_x$ ) to the incident wave polarisation can be written in the form

$$\Delta K_q(t) = \left[ \sigma_c N_c(t) + \int n_t(\Omega, t) (S^{-1} \hat{\sigma}_t S)_{qq} d\Omega - \frac{1}{3} \sigma_t N_0 \right] d, \quad (6)$$

$$q = x, z,$$

where  $S$  is the matrix of the transfer from the coordinate system bound with the trans-isomer molecule to the system bound with the sample. If we assume that all the trans isomers participate in the trans–cis isomerisation process, then, using expansion (3), the change in the optical density can be presented in the form

$$\begin{aligned}\Delta K_z(t) &= 3K_0 \left\{ \left( \alpha - \frac{1}{3} \right) [1 - \bar{T}_0(t)] + \frac{2}{15} \bar{T}_2(t) \right\}, \\ \Delta K_x(t) &= 3K_0 \left\{ \left( \alpha - \frac{1}{3} \right) [1 - \bar{T}_0(t)] - \frac{1}{15} \bar{T}_2(t) \right\},\end{aligned}\quad (7)$$

where  $\alpha = \sigma_c/\sigma_t$ . Note that only two lowest expansion coefficients (3) averaged over the sample thickness enter expression (7).

The first term in (7) corresponds to the isotropic part of a change in the optical density, which is caused by the appearance of cis-isomers. The contribution of the isotropic part at the stage of the optical action, as one can see from (7), is determined by the ratio of the absorption cross section of cis and trans isomers (the quantity  $\alpha$ ) for the probe radiation and positive in the case  $\alpha > 1/3$ . The second term reflects the influence of the trans-isomer distribution anisotropy. Because  $\bar{T}_2(t) < 0$ , the contribution of the anisotropy part is positive for  $\Delta K_x(t)$  and negative for  $\Delta K_z(t)$ . If the concentration of the cis isomers is small ( $\bar{T}_0 \approx 1$ ), i.e., the rate of the cis–trans isomerisation and the spontaneous decay time of the cis isomers are small, we can neglect the isotropic component and  $\Delta K_z(t) \approx -2\Delta K_x(t)$ . In another limiting case, when the concentration of the cis isomers is large ( $\bar{T}_0 \approx 0$ ) and  $\alpha \gg 1$  for rather large irradiation doses, we have  $\Delta K_z(t) \approx \Delta K_x(t) > 0$ . In intermediate cases, depending on the quantity  $\alpha$ , the functions  $\Delta K_x(t)$  and  $\Delta K_z(t)$  can be nonmonotonic.

For the change rate of the quantities  $\Delta K_x(t)$  and  $\Delta K_z(t)$  immediately after switching on the incident radiation, we can obtain from (4) and (7) the expressions [5]:

$$\left. \frac{d\Delta K_z}{dt} \right|_{t=0} = (\alpha - 0.6)a_t I_0 (1 - e^{-K_0}), \quad (8)$$

$$\left. \frac{d\Delta K_x}{dt} \right|_{t=0} = (\alpha - 0.2)a_t I_0 (1 - e^{-K_0}).$$

The sign of the change rate of these quantities at the instant of switching on the incident radiation depends, as follows from (8), on the ratio of the absorption cross sections of cis and trans isomers  $\alpha$ .

The experimentally measured changes in the optical density of probe radiation polarised parallel and perpendicular to incident radiation allow one to reconstruct the dynamics of the expansion coefficients  $\bar{T}_0$  and  $\bar{T}_2$  averaged over the sample thickness:

$$\bar{T}_0(t) = 1 - \frac{\Delta K_z(t) + 2\Delta K_x(t)}{9(\alpha - 1/3)K_0}, \quad \bar{T}_2(t) = \frac{\Delta K_z(t) - \Delta K_x(t)}{1.6K_0}. \quad (9)$$

The key moment in the comparison of the experimental results with the results of model calculations as in paper [5] was the assumption that only a part of trans isomers (with the concentration  $N_a$ ), which we will call active, participates in the trans–cis isomerisation process and contributes to the

dichroism. This can be illustrated by the example when the concentration of the cis isomers can be neglected ( $\bar{T}_0 = 1$ ). In this case, only the trans-isomer distribution anisotropy contributes to the dichroism and  $\Delta K_z(t) = -2\Delta K_x(t) = \frac{2}{5}\bar{T}_2(t)K_0$ . In this case, calculated and experimental dependences coincide if we introduce the multiplier  $\xi < 1$  in expression (7) in front of  $K_0$ , i.e., only a part of trans isomers contributes to the dichroism. The authors of paper [5] suggested that the impossibility for the trans isomers to become the cis isomers can be explained by the absence of a rather free volume [4, 18, 19]. For this inactive trans isomer, the energy acquired during the photon absorption can dissipate through the cascade of rotational–vibrational transitions [20, 21]. We will assume that the trans isomers not participating in the trans–cis isomerisation processes do not change orientation during the light absorption. However, within the framework of the proposed model, their orientation changes due to the interaction with the polymer matrix in the case of the mutual orientational diffusion. This process is secondary because the reorientation of the active trans isomers under the action of light leads to the reorientation of the polymer matrix fragments, which, in turn, leads to the reorientation of the inactive trans isomers. The model calculations showed that in the absence of the initial anisotropy, the contribution of the inactive trans isomers to the dichroism can be neglected at times smaller than the time required to achieve the stationary state.

Therefore, in expressions (7)–(9) it is necessary to use  $K_0 = \xi K$ , where  $K$  is the experimentally measured optical density of the unirradiated sample, and  $\xi = N_a/N_0$  is the fraction of the trans isomers participating in the trans–cis isomerisation process. The coefficient  $\xi$  was estimated by the results of the comparison of the experimental data with the calculated ones.

### 3. Experimental

In this paper, we studied the dynamics of the light-induced dichroism for different amorphous azopolymers (P1–P4). Polymer P1 is a mixture of PMMA with 4-4'-oxycyanobenzene (OCAB-6M) with the 0.5% mass concentration of the azo dye [22]. Polymer P2 is a copolymer [16] consisting of a photochromic group (4-4'-oxycyanobenzene with the molar concentration of 10%) and mesogenic group (4-4'-oxycyanobiphenyl with the molar concentration of 90%). In polymer P2, unlike P1, the photochromic and mesogenic fragments are functionally bound with the main chain with the help of 'spacer' [(CH<sub>2</sub>)<sub>2</sub> group]. Polymers P3 and P4 are homopolymers {4-[(methacryloyloxyalkylene)methylamino]-4-X azobenzene} with the 100% content of the azo dye. In polymer P3 we have a substituent X = NO<sub>2</sub> [23], and in polymer P4 we have X = CH<sub>3</sub> [24].

The dye entering the composition of P1 and P2 polymers belongs to the azobenzene dyes. In these dyes the lifetime of a cis isomer is comparatively large [4, 17]. Homopolymers P3 and P4 belong to the aminoazobenzene dyes. The physical properties of such azopolymers (absorption spectra, the cis-isomer lifetime) substantially depend on the degree of the X substituent polarity. We considered two limiting cases: a strongly polar substituent (X = NO<sub>2</sub>, polymer P3) and a nonpolar substituent (X = CH<sub>3</sub>, polymer P4). Each polymer was represented by two samples with different optical densities.

The samples were irradiated by linearly polarised radiation from the diode-pumped 532-nm solid-state LCS-DTL-318 laser. The induced dichroism was measured with probe radiation at the same wavelength from the solid-state LCM-S-111 laser modulated at the frequency 1.5 kHz. The polarisation plane of probe radiation was rotated with a  $\lambda/2$  plate. By using synchronous detection and monitoring of probe radiation, we measured the optical density with an accuracy of 0.2%. Before the measurements, the samples were thermally treated: heated for one hour up to the temperature 145 °C (polymers P1 and P2) and 130 °C (polymers P3 and P4) and then cooled for one hour. The experiments showed that, despite the thermal treatment, some samples retained insignificant dichroism.

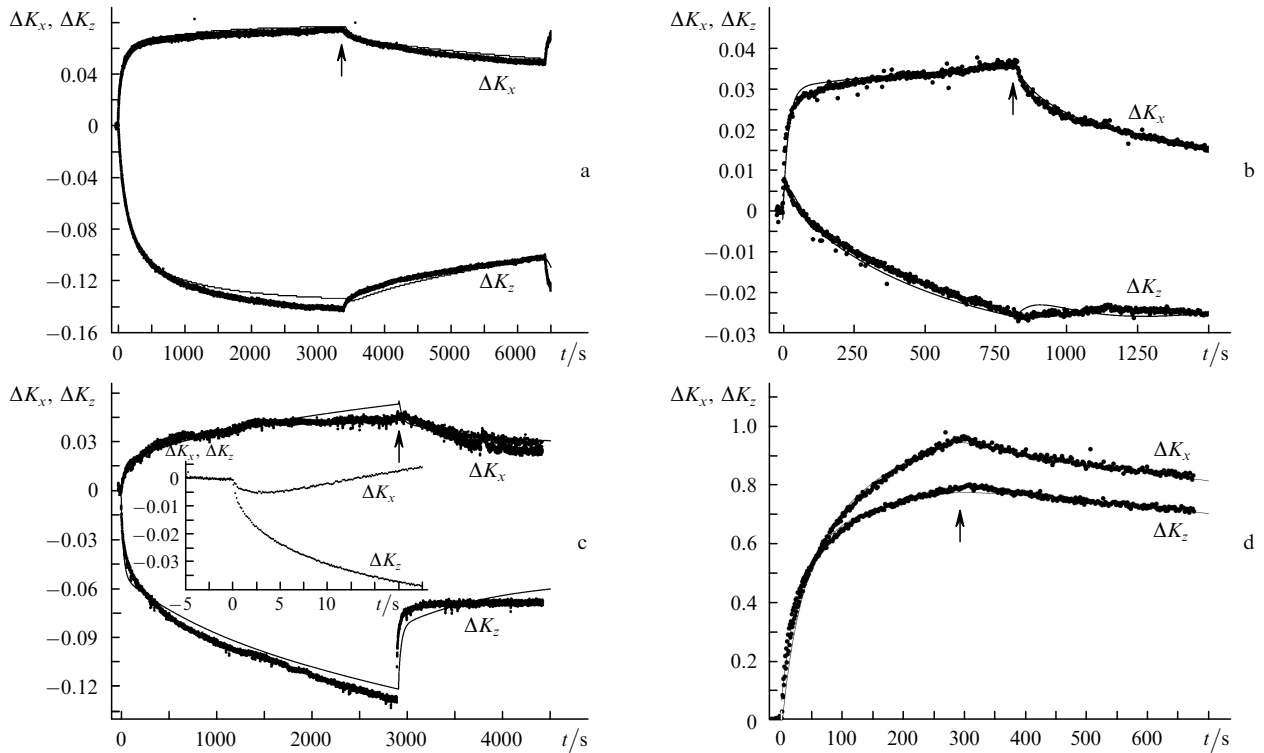
Figure 2 presents the experimental time dependences of the change in the optical density  $\Delta K_z$  and  $\Delta K_x$  during irradiation, which were measured with probe radiation polarised parallel and perpendicular to incident radiation, for P1–P4 polymers.

The experimental results were processed and compared with the theoretical results by using the program simulating the system of equations (4) for the coefficients  $\bar{T}_n(t)$ ,  $\bar{F}_n(t)$  up

to the six order inclusively and the samples with a high optical density. Analysis showed that the account for the higher-order expansions is insignificant. The optical chromophore parameters used in this paper were estimated based on the experimental dependences of  $\Delta K_z(t)$  and  $\Delta K_x(t)$  in several steps. The obtained estimates are listed in Table 1.

Let us explain the processing sequence by the example of polymer P1. The trans-isomer absorption cross section  $\sigma_t$  was estimated by the optical density of the unirradiated sample under assumptions that the trans isomers are isotropically distributed over the angles,  $K = \beta d$  ( $\beta = \frac{1}{3}\sigma_t N_0$ ), and the contribution to absorption from the polymer matrix can be neglected. The latter assumption is justified because the measurements are performed in the absorption region of the chromophores and in the transparency region of the polymer matrix. The concentration  $N_0$  of the trans isomers was assessed by the azopolymer structural formula. In this case, the azopolymer density was assumed equal to 1.3 g cm<sup>-3</sup> and the same for all types of the polymers.

The ratio of the cis- and trans-isomer absorption cross



**Figure 2.** Dynamics of the optically induced dichroism  $\Delta K_x$  and  $\Delta K_z$  for azopolymers P1 (a), P2 (b), P3 (c), and P4 (d) at the irradiation intensities 26 (a), 21 (b), 16 (c), and 21 mW cm<sup>-2</sup> (d). Points are the experiment, thin solid curves are the calculations with the help of parameters listed in Table 1. The inset shows the initial segments of the dependences  $\Delta K_x(t)$  and  $\Delta K_z(t)$  for polymer P3. The arrows show the instants of switching on incident radiation.

**Table 1.** Azopolymer parameters estimated from the experimental data by the optically induced dichroism.

Polymer	$N_0/10^{20}$ cm <sup>-3</sup>	$K$	$\beta_0/$ cm <sup>-1</sup>	$\sigma_t/10^{-18}$ cm <sup>2</sup>	$\sigma_c/\sigma_t$	$\gamma_t$	$\gamma_c/\gamma_t$	$\tau_c$	$\xi$	$D_1/$ 10 <sup>-4</sup>	$D_2/$ 10 <sup>-4</sup>	$D_3/$ 10 <sup>-4</sup>
P1	0.4	1.21	15.5	1.2	0.44 ± 0.02	0.45 ± 0.1	1.6 ± 0.2	20 ± 5	0.20 ± 0.02	1.5	1.0	–
P2	2.5	0.3	120	1.4	0.7 ± 0.05	0.2 ± 0.05	1.4 ± 0.2	300 ± 50	0.30 ± 0.04	22	5.5	–
P3	21	3.5	1.8 × 10 <sup>4</sup>	25	0.02 ± 0.005	0.02 ± 0.01	–	3 ± 0.5	0.20 ± 0.02	50	2	1
P4	23	4.14	8.5 × 10 <sup>3</sup>	11	10.0 ± 1.0	0.0045 ± 0.001	2 ± 0.4	3000 ± 300	0.60 ± 0.05	8.5	0.1	–

Note: In the experiments, the incident radiation intensities of 5–850 mW cm<sup>-2</sup> were used for polymers P1, P4 and 5–26 mW cm<sup>-2</sup> for P2, P3.

sections  $\alpha$  was estimated by the rate of the change of the quantities  $\Delta K_z$  и  $\Delta K_x$  immediately after switching on irradiation when we can assume that  $\bar{T}_0 = 1$  and  $\bar{T}_2 = 0$ . It follows from (8)

$$\alpha = \left( \left. \frac{dK_z}{dt} \right|_{t=0} - 3 \left. \frac{dK_x}{dt} \right|_{t=0} \right) \left( \left. \frac{dK_z}{dt} \right|_{t=0} - \left. \frac{dK_x}{dt} \right|_{t=0} \right)^{-1}.$$

The obtained parameters were used in simulating the dynamics of the optically induced dichroism.

At the next stage, we used the following basic fitting parameters  $a_1 I_0$ ,  $\xi$ , and the diffusion coefficients  $D_1$ ,  $D_2$ . The parameter  $a_1 I_0$  was chosen so that the experimental and calculated rates of changes in  $\Delta K_z$  and  $\Delta K_x$  would coincide immediately after switching on incident radiation. Because the intensity  $I_0$  of radiation affecting the sample is known, the quantum yield of the trans–cis isomerisation process (see Table 1) is found by using the parameter  $a_1 I_0$ . The results of fitting the parameters  $D_1$ ,  $D_2$ , and  $\xi$  are presented in Fig. 2a.

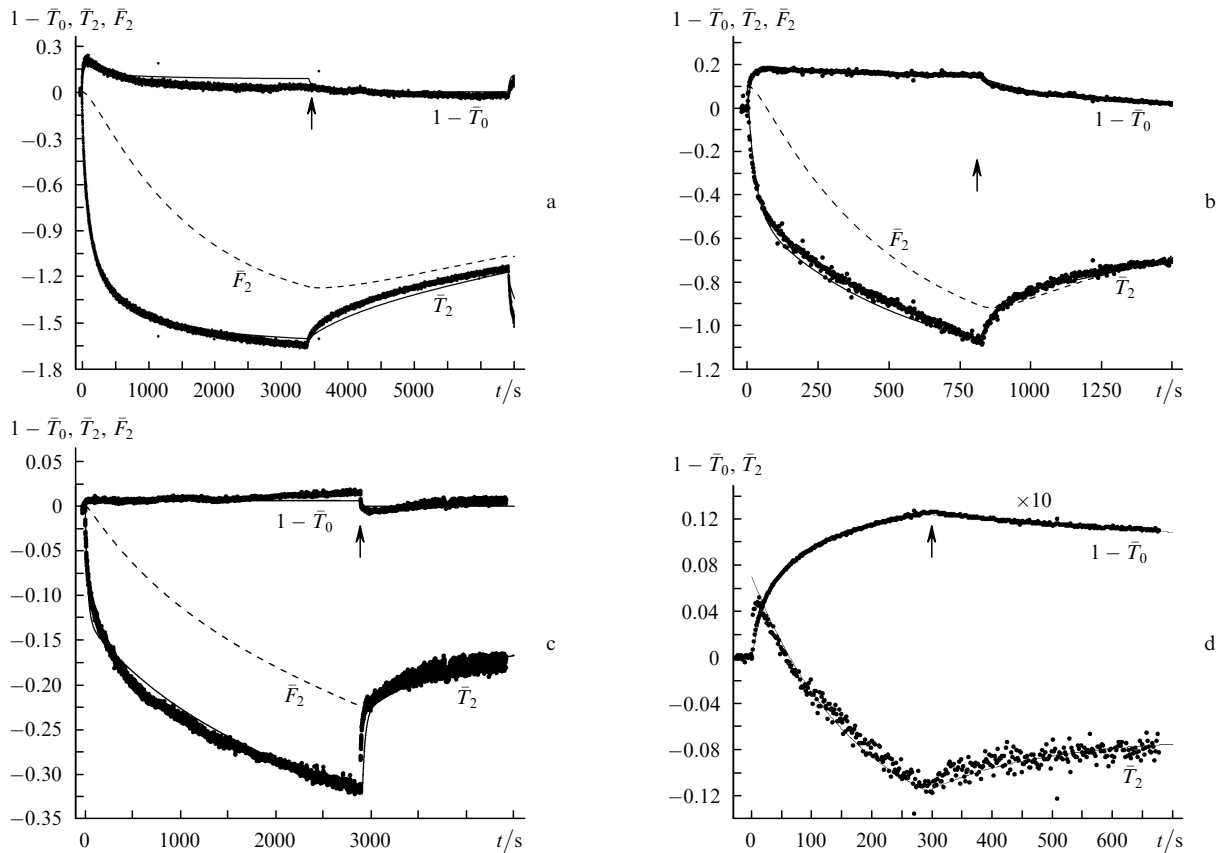
The parameters  $a_c/a_t$  and  $\tau_c$  most strongly affect the dynamics of the cis-isomer concentration. Therefore, we estimated them by using the model and experimental dependences, calculated using expressions (9), of the expansion coefficients  $\bar{T}_0(t)$  and  $\bar{T}_2(t)$  averaged over the sample thickness (Fig. 3a). One can see from Fig. 3a that the relative concentration of the cis isomers varies depending on the irradiation time nonmonotonically, achieving the

maximum value  $(1 - \bar{T}_0)_{\max}$ . By assuming that  $(1 - \bar{T}_0)_{\max} = (1 + 0.3/A)^{-1}$ , we obtain

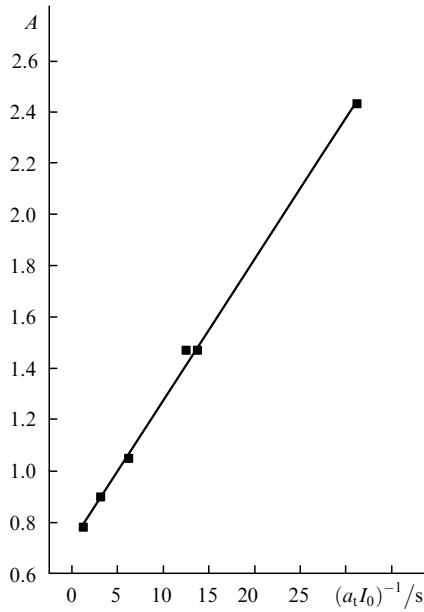
$$A = 0.3[(1 - \bar{T}_0)_{\max}^{-1} - 1] = \frac{a_c}{a_t} + \frac{1}{\tau_c a_1 I_0}.$$

Thus, by studying the dependence of  $(1 - \bar{T}_0)_{\max}$  on the irradiation intensity, we can find the estimates of the parameters  $\gamma_c/\gamma_t$  and  $\tau_c$ . Figure 4 shows the values of the parameter  $A$  calculated by the experimentally measured values of  $(1 - \bar{T}_0)_{\max}$  for different irradiation intensities  $I_0$  and the approximating straight line used to assess the ratios  $\gamma_c/\gamma_t$  and  $\tau_c$  listed in Table 1. The model time dependence of  $1 - \bar{T}_0$  obtained by using these parameters coincides with the experimental one at  $t < 1000$  s (see Fig. 3a). In our opinion, the difference at large times is caused by the dynamics of the initial anisotropy, which was present in the sample. Figure 3a demonstrates also the model and experimental dependences of  $\bar{T}_2(t)$ , which almost coincide at the stage of irradiation and slightly differ at the stage of relaxation. The angular distribution anisotropy  $\bar{F}_2$  of the matrix (the dashed curve in Fig. 3a) both at the stage of irradiation and relaxation is determined by the ratio of the diffusion coefficients  $D_1$  and  $D_2$ .

One can see from Figs 2a and 3a that the proposed simple model of the chromophore–polymer matrix interaction in the case of polymer P1 satisfactorily describes the experimental dependences both at the stages of irradiation and relaxation after switching off irradiation, and allows one to estimate the main optical parameters of the



**Figure 3.** Dynamics of the isotropic  $[1 - \bar{T}_0(t)]$  and anisotropic  $[\bar{T}_2(t)]$  parts of the dichroism calculated from the experimental data by using expressions (9) (points) and according to the theoretical model (thin solid curves) for azopolymers P1 (a), P2 (b), P3 (c), and P4 (d). The dashed curves are the dynamics of the polymer matrix anisotropy  $\bar{F}_2$ .



**Figure 4.** Dependence of the parameter  $A = 0.3[(1 - T_0)_{\max}^{-1} - 1]$  on the inverse rate of trans–cis isomerisation  $a_t I_0$  for azopolymer P1. Points are the experiment, solid line is the model dependence.

chromophores. The processes proceeding during the interaction of the chromophores with the polymer matrix at both stages are rather complicated and diverse and, in particular, depend on the rigidity of the main chain and spacers, the way the chromophore fragments are ‘attached’ [15], etc. Therefore, sometimes the dynamics of the photoinduced dichroism and birefringence is described with the help of the Kohlrausch–Williams–Watts function [25, 26], which implicitly takes into account the existence of the continuous spectrum of the characteristic times. The manifestation of this, in the case of the azopolymer P1, was the dependence of the fitting diffusion coefficient  $D_2$  on the irradiation time, the coefficient  $D_1$  being invariable.

The estimates of  $\sigma_t$  for polymers P1 and P2 differ insignificantly (see Table 1), which is obviously caused by the use of the same dye in these polymers. An increase in the components  $\Delta K_z(t)$  and  $\Delta K_x(t)$  immediately after switching on incident radiation (see Fig. 2b) corresponds, as follows from (8), to the parameter  $\alpha = 0.7$ . At  $t < 70$  s, the isotropic part of  $\Delta K_z(t)$  exceeds the anisotropic component, which leads to the positive  $\Delta K_z(t)$ . The maximum concentration of cis isomers in polymer P2 was 20 % (see Fig. 3b). The decay of cis isomers whose lifetime for polymer P2 is 300 s makes a significant contribution to the trans-isomer relaxation after switching on incident radiation.

The nonmonotonic dependence  $\Delta K_x(t)$  after switching on incident radiation in the case of polymer P3 is shown in the inset of Fig. 2c and is caused by the small  $\alpha$  equal to 0.02. For the satisfactory fit of the calculated dependences to the experimental ones, we had to modify the polymer matrix model. We assumed that the polymer matrix can be represented in the form of two fragments F and F1 described by the distribution functions  $f(\Omega, t)$  and  $f_1(\Omega, t)$ . In this case, the fragment F interacts directly with the chromophores, while the fragment F1 interacts only with the fragment F. By assuming that the interactions have a character of the mutual orientational diffusion, equation (2b) for  $f(\Omega, t)$  can be replaced by the equations

$$\begin{aligned} \frac{\partial f(\Omega, t)}{\partial t} &= D_2 \Delta_{\Omega} \left[ f(\Omega, t) - \frac{n_t(\Omega, t)}{\int n_t(\Omega, t) d\Omega} \right] \\ &+ D_3 \Delta_{\Omega} [f(\Omega, t) - f_1(\Omega, t)], \\ \frac{f_1(\Omega, t)}{\partial t} &= D_4 \Delta_{\Omega} [f_1(\Omega, t) - f(\Omega, t)]. \end{aligned}$$

The results of fitting for polymer P3 by this modified model are presented in Fig. 2c. A significant discrepancy between the experimental and calculated dependences, especially in the relaxation region, is obviously caused, in the case of polymer P3, by a more complex mechanism of the chromophore–matrix interaction, which is not described by the modified model. Figure 3c presents the model dependences and dependences of the coefficients  $\bar{T}_0(t)$  and  $\bar{T}_2(t)$  averaged over the sample thickness, the latter dependences being calculated by expressions (9) using the experimental data. The lifetime of cis isomers estimated by using the dependence  $\bar{T}_0(t)$  was 3 s, the concentration of cis isomers for the 26-mW  $\text{cm}^{-2}$  intensity did not exceed 1 %. The small lifetime of the cis isomers did not allow us to obtain an estimate for the parameter  $\gamma_c/\gamma_t$ .

The qualitative analysis of the absorption dynamics for polymer P4 (see Fig. 2d) allows the following conclusions to be made. First, the ratio of the absorption cross sections of the cis and trans isomers are larger than 0.6 because first we observe an increase in  $\Delta K_x(t)$  and  $\Delta K_z(t)$  as in the case of polymer P2. Second, at the initial stage of irradiation, the change in the absorption is mainly determined by the isotropic part and by the appearance of the cis isomers. As the irradiation dose rises, the contribution to the absorption of the anisotropic part of the trans-isomer distribution becomes greater and the difference between the absorption of probe radiation with parallel and perpendicular polarisations increases.

It is difficult to assess the concentration of the cis isomers during the irradiation by the shape of the time dependences of the absorption coefficients; however, the role of these isomers becomes evident at the stage of relaxation, after switching off irradiation. For this azopolymer, the lifetime of the cis isomers is crucial for the relaxation process and is about 3000 s. After switching off the irradiation and the decay of the cis isomers, the isotropic part of the optical density should become the same as before the irradiation. Having measured the absorption of radiation with parallel and orthogonal polarisations two days later, we observed this phenomenon experimentally. In this case, the sample was characterised by insignificant induced anisotropy of the absorption. Note one more peculiarity of the absorption dynamics for polymer P4. In the initial state, we observed an insignificant anisotropy of the sample:  $K_z(0) \neq K_x(0)$ . This initial anisotropy is manifested in the fact that at  $t < 50$  s, the dependence  $\Delta K_z(t) = K_z(t) - K_z(0)$  lies higher than the dependence  $\Delta K_x(t)$ .

The estimate of the trans-isomer absorption cross section  $\sigma_t$  for polymer P4, obtained by measuring the absorption of the unirradiated sample, is given in Table 1. The preliminary estimates ( $\alpha = 13.4$  and  $\gamma_t = 0.02$ ) were obtained by using the initial segment of the dependences  $\Delta K_z(t)$  and  $\Delta K_x(t)$  with the help of expression (7) at  $\xi = 1$ . Note that expression (7) neglects the initial optical anisotropy, which is present in our sample. We preliminarily estimated the ratio  $a_c/a_t$  by

using the exponential approximation of the experimentally measured isotropic part of the change in the optical density under the assumption that the trans-isomer lifetime is large and its influence on the obtained estimate can be neglected.

We used the preliminary estimates as initial during the fitting process in simulations of system (4). The results of the fitting are presented in Figs 2d, 3d and in Table 1. In simulations we took into account the initial anisotropy of the sample by assuming that  $T_2(0) = F_2(0) = 0.07$ . The decay time of the cis isomers assessed by the relaxation curve was 3000 s. The relative concentration of the cis isomers during the irradiation time  $t = 300$  s virtually achieves a maximum value of 1.5% (see Fig. 3d). The low fraction of the cis isomers is caused by the high rate of the cis–trans isomerisation compared to the rate of the trans–cis isomerisation ( $a_c/a_t = 20$ ) and weakly depends on the cis-isomer lifetime [ $(a_t I_0 \tau)^{-1} = 0.1$ ]. The obtained good agreement between the experimental and calculated dependences for polymer P4 (see Figs 2d and 3d) is obviously explained by the relatively weak influence of the polymer matrix in the irradiation doses under consideration.

The data listed in Table 1 for polymers P1 and P2 are basically close to the results of papers [17, 24, 27, 28]. Thus, the authors of papers [27, 28] obtained the following values for the quantum yield  $\gamma_t$  of the trans–cis isomerisation process and the ratio  $\gamma_c/\gamma_t$ :  $\gamma_t = 0.2 - 0.36$  [28] and  $0.23$  [27],  $\gamma_c/\gamma_t = 2$  [24, 28]. The largest discrepancy is observed for the absorption cross section ratio:  $\sigma_c/\sigma_t = 2.0$  [4],  $2.8$  ( $\lambda = 450$  nm), and  $2.1$  ( $\lambda = 488$  nm) [24]. Obviously, this discrepancy, as the ratio  $\gamma_c/\gamma_t$ , is caused by the difference in the structures of the azo dyes. In polymers P1 and P2, the dye is oxycyanoazobenzene, while in papers [17, 24, 27, 28] azobenzene was used. In addition, the results presented in Table 1 correspond to  $\lambda = 532$  nm, while according to [24, 28], the ratio  $\sigma_c/\sigma_t$  decreases with increasing the wavelength. This can explain the fact that for polymers P1 and P2 we obtained  $\sigma_c/\sigma_t < 1$  (see Table 1).

The difference in the cis-isomer lifetimes as well as in the parameters  $\gamma_t$  for polymers P1 and P2 is obviously caused by the different azopolymer structure. As was shown above, polymer P1 is a mixture of a dye and PMMA. In polymer P2, the dye enters into the composition of the copolymer, which complicates the trans-to-cis transition, and vice versa.

The azo dyes entering into the composition of the polymers under study have two characteristic absorption regions caused by the electronic transitions  $\pi - \pi^*$  and  $n - \pi^*$  [17, 27]. Absorption in the region of the  $\pi - \pi^*$  transition is at least an order of magnitude greater than absorption in the region of the  $n - \pi^*$  transition. In polymers P1, P2, the region of the  $\pi - \pi^*$  transition corresponds to  $\lambda = 320 - 360$  nm (trans isomer) and  $\sim 200$  nm (cis isomer) [27], while the region of the  $n - \pi^*$  transition corresponds to  $\lambda = 440 - 460$  nm (for cis and trans isomers this region is the same). In polymers P3, P4, which belong to the class of aminoazobenzenes, the situation is somewhat different. Here, all depends on the degree of the X substituent polarity [17]. If the substituent is nonpolar, for example hydrogen H or methyl  $\text{CH}_3$ , the absorption spectrum of the azo dye will be close to the spectrum of the dye in polymers P1 and P2. When the degree of the X substituent polarity is increased, the region of the  $\pi - \pi^*$  transition is shifted to the red and at  $\text{X} = \text{NO}_2$  (the maximum degree of the polarity) overlaps the region of the  $n - \pi^*$  transition. The absorption band in this case can

occupy the region  $\lambda = 460 - 500$  nm [25]. The degree of the substituent polarity does not produce any significant effect on the spectral parameters of the cis isomer in the region of the  $n - \pi^*$  transition [29]. This can explain so small value of  $\sigma_c/\sigma_t$  for polymer P3 compared to other polymers under study, because for this polymer the exciting radiation wavelength  $\lambda = 532$  nm corresponds to the  $n - \pi^*$  transition in the cis isomer and  $\pi - \pi^*$  transition in the trans-isomer.

The obtained estimates for the cis-isomer lifetime  $\tau_c$  (see Table 1) correspond to the data published in paper [30] and review [17]. According to [17], the lifetime  $\tau_c$ , as the spectral characteristics of absorption, significantly depend on the degree of the X substituent polarity in the azo dye. If the substituent is nonpolar, the cis isomer can have a very long lifetime (up to ten days [30]). In the case of the polar substituent (polymer P3), the lifetime  $\tau_c$  is significantly smaller (from milliseconds in the solution up to several seconds in the polymer film [17]). The azo dyes entering into the composition of polymers P1 and P2, although belong to the class of azobenzenes, contain a polar substituent (cyano group CN with respect to the polarity degree occupies an intermediate position between  $\text{NO}_2$  and  $\text{CH}_3$ ). Obviously, it explains the fact that the values of  $\tau_c$  for polymers P1 and P2 are larger than for P3, and smaller than for P4 (see Table 1).

The quantum yield  $\gamma_t$  of the trans–cis isomerisation process for polymers P3 and P4 presented in Table 1 is close to the results of paper [4]. The quantum yield  $\gamma_t$  for polymers P1 and P2 is significantly higher than for P3 and P4. Obviously, this is caused by the presence of the amino group in the composition of the azo dyes in polymers P3 and P4.

In polymer P4, the fraction of the trans isomers participating in the trans–cis isomerisation processes proved the highest ( $\xi = 0.6$ ). This indirectly confirms the fact that the dipole interaction between the azo dye molecules [31] plays also an important role in the trans–cis isomerisation process along with the steric factor (critical free volume [4, 25]).

## 4. Conclusions

We have proposed the photoorientation model in azopolymers in which the chromophore–polymer matrix interaction is described within the framework of the mutual orientational diffusion. We have shown that for the four types of the amorphous azopolymers the model satisfactorily describes the dynamics of the optically induced absorption anisotropy both in the process of the light action and at the stage of relaxation after switching off the irradiation. We have found that only a part of the azopolymer (trans isomers with a sufficient free volume) participates in the trans–cis isomerisation process and contributes to the formation of the optically induced dichroism.

We have demonstrated the possibility to estimate, by measuring the dynamics of the optically induced dichroism, the optical parameters of the azopolymers and the parameters of the mutual diffusion describing the interaction of the trans isomers with the polymer matrix. The found optical parameters (absorption cross sections and quantum yields of trans and cis isomers, the lifetime of the cis-isomers) for the azopolymers under study well agree with the results of the previously published papers.



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