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Kinetic characteristics of light induced anisotropy and mechanisms of the molecular alignment in azo dye containing polymer films

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Induction and relaxation of optical anisotropy in azobenzene containing polymer films under the action of polarized UV-light irradiation are investigated by polarization UV and IR spectroscopy methods. The dependence of anisotropy relaxation on the exposure conditions is established. The results are interpreted supposing the partial ordering of main-chains fragments in irradiated films. A theoretical model explaining experimental results is developed.

Keywords: photoinduced optical anisotropy, azo dye containing polymer

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INTRODUCTION

Effect of photoinduced optical anisotropy (POA) is widely studied in the last ten years. Materials displaying POA seem highly perspective for optical information recording and storage^[1-2] as well as for an alternative way of liquid crystal orientation^[3-7]. In general, POA may be in such a polymer for which a photochemical reaction sensitive to the polarization of irradiating light takes place. Polymers containing chemically bounded dichroic dyes are the most widely used for POA. As strongly dichroic dyes, azobenzene derivatives are often utilized. Polymers containing azobenzene dyes are likely to be the most efficient for POA. Photoinduced birefringence in these polymers reaches values as high as 10^{-1} .

It is supposed that optical anisotropy in films of these polymers is due to photoinduced alignment of dye fragments^[8]. If dyes are strongly dichroic, then in the electro-magnetic field of light as a result of multiple acts of light absorption followed by deactivation of the excited state, they reorient in such a way that their optical dipole moments become perpendicular to the direction of polarization of the exciting light and light absorption reaches minimum.

For applications of POA, characteristics of anisotropy recording and its relaxation are very important. Comprehensive analysis of the literature devoted to POA effect brought out that polymers having similar absorbing fragments display essentially different recording and relaxation features. For example, in^[9] it is reported about full relaxation of POA in azo dye containing a polymer while in^[10] only partial relaxation was observed for the similar polymer. On the other hand, in^[11] increasing of alignment of azo dye molecules in a LB film was observed after switching off of a pumping light. It is apparently that the simple assumption about light induced

alignment of photosensitive fragments of polymer molecules is insufficient for adequate interpretation of all observed features of POA.

The aim of our work was to study characteristics of POA recording and its relaxation in thin films of azo dye containing a polymer and to determine how the kinetics of the relaxation depends on the processes of molecular fragments ordering in films.

EXPERIMENT

Materials

The structure formula of the azo polymer we used is presented in Fig. 1. Its

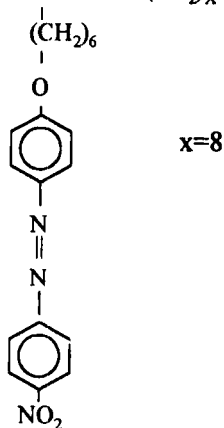
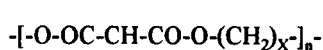


FIGURE 1.

synthesis is described elsewhere ^[12]. This polymer absorbs light with $\lambda < 500$ nm due to a azobenzene chromophore contained in the side-chains of polymer molecules. An optical dipole moment of the *trans* isomer is oriented almost along its long axis ^[13] and is equal 9.3 ^[14]. So *trans* isomers oriented parallel to the vector **E** of a linearly polarized light absorb light more intensively than those oriented perpendicularly. When exposed to UV-light, azobenzene chromophores undergo

reversible *trans-cis*-photoisomerization and reorient in space. Finally, due to the mechanism described above, all azobenzene chromophores are oriented perpendicularly to the vector **E** of light and an anisotropy is induced with the extraordinary axis of the samples parallel to the azobenzene chromophores orientation.

In our investigations, thin films of the azo polymer were spincoated on quartz or NaCl plates from a polymer solution in dichloroethane (10 g/l). Thickness of the films obtained was about 50-100 nm. A high pressure Hg-lamp (10 mWt/cm²) was used for POA induction. A Glan-Thomson prism was utilized to polarize the exciting light. UV spectra were measured in the range 200-500 nm with spectrometer KSVU (LOMO, St.-Petersburg). IR polarization spectra were recorded on FIR-88 Bruker Spectrometer with resolution of 2 cm⁻¹ and accumulations 32 scans in the spectral region from 4000 to 600 cm⁻¹.

Experiment and discussion

To study the prepared polymer films, we used UV and IR spectroscopy as

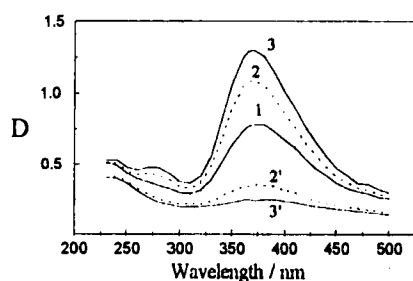


FIGURE 2.

well as birefringence measurements. An absorption spectrum of a non-irradiated film is shown in Fig. 2 (curve 1). The film is optically isotropic. After enduring irradiation, the absorption spectrum of the film becomes anisotropic because of azobenzene fragments reorientation perpendicular to the direction of polarization of the exciting beam. Curves 2 and 2' in Fig. 2 present absorption spectra of the film D_{\parallel} and D_{\perp} when a direction of the testing beam polarization is parallel or perpendicular to the direction of the azobenzene chromophores orientation. These spectra were measured at once after film irradiation during 15 min. After relaxation in dark during 30 min, a dichroism of the film increases (curves 3 and 3' in Fig. 2). This result indicates further "dark" ordering in the polymer film and has been first observed in LB-films^[11]. So we decide

to investigate the kinetics of photoanisotropy induction and its relaxation. It turns out that the type of relaxation depends on the time of irradiation. In Fig. 3, we have shown the dependences of D_{\parallel} and D_{\perp} versus the time of irradiation as well as relaxation curves

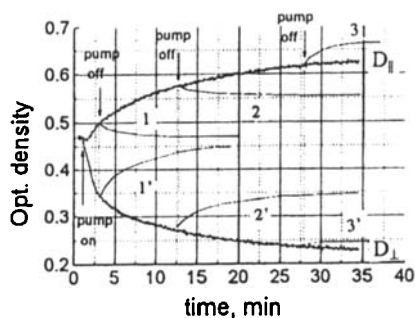


FIGURE 3.

after the irradiation switching off at various moments of POA induction. It is seen that for the short time there is only the reversible component (1, 1'). With exposure increasing, an irreversible component appears (2, 2'). "Dark" ordering was observed only for the component D_{\parallel} and only for the long time of irradiation (3,3').

A simple mechanism of POA described above does not explain the whole variety of relaxation characteristics. To describe them we have to take into

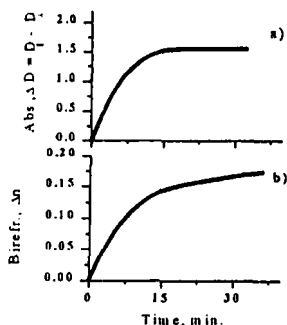


FIGURE 4.

account the interaction of azobenzene fragments with the polymer matrix.

However, it is difficult to explain both reversible and irreversible POA recording in the same matrix. We suppose that the polymer matrix also changes during irradiation. To check this assumption, the kinetic curves of $\Delta D = D_{\parallel} - D_{\perp}$ and birefringence Δn

recording were measured simultaneously (Fig. 4). It is seen that Δn grows slowly while ΔD is already saturated. Since ΔD is defined due to

TABLE

ν , cm^{-1}	Band Assignment	Structural Origin	Dichroic ratio, $R=\alpha_{\parallel}/\alpha_{\perp}$
2930	$\nu_{\text{as}}(\text{CH}_2)$	main chain/side chain	0.41
2855	$\nu_{\text{s}}(\text{CH}_2)$	main chain/side chain	0.35
1748	$\text{Q}(\text{C}=\text{O})$	main chain	0.22
1731	$\text{Q}(\text{C}=\text{O})$	main chain	0.24
1603	$\text{Q}(\text{C}-\text{C})$	azobenzene chromophore	3.0
1581	$\text{Q}(\text{C}-\text{C})$	azobenzene chromophore	4.25
1524	$\text{Q}_{\text{as}}(\text{NO}_2)$	azobenzene chromophore	0.1
1507	$\text{Q}(\text{C}-\text{C})$	azobenzene chromophore	2.25
1501	$\text{Q}(\text{C}-\text{C})$	azobenzene chromophore	4.4
1342	$\text{Q}_{\text{s}}(\text{NO}_2)$	azobenzene chromophore	4.3
1257	$\text{Q}_{\text{as}}(\text{C}-\text{O}-\text{Ar})$	azobenzene chromophore	4.5
1202	$\text{Q}(\text{C}-\text{CO}-\text{O}-)$	main chain	1.25
1142	$\text{Q}(\text{N}-\text{Ar})$	azobenzene chromophore	4.0
1107	$\text{Q}(\text{C}-\text{CO}-\text{O}-)$	main chain	1.43

azobenzene chromophores absorption and Δn due to all fragments of polymer molecules, it is clear that not only azobenzene chromophores but other fragments of polymer molecules take part in orientational ordering. An arrangement time of some nonabsorbing fragments of molecules could be greater than that one of azobenzene chromophores. As a result, the difference in the recording kinetics of ΔD and Δn is observed.

It is reasonable to suppose that a long characteristic time of the curve $\Delta n(t)$ corresponds to the main-chain fragments arrangement because its conformational mobility is lower than that for azobenzene chromophores. Polarization IR spectra of the films with POA confirm our assumption about partial chain fragments ordering. It was found that IR bands as of the

azobenzene chromophores as well as the main-chain fragments are polarized (see Table). Polarization of the main-chain bands indicates that some fragments of the main-chain are oriented in the direction of the azobenzene chromophores orientation. It may be when main-chain fragments are stretched in elongated loops in that direction. Details analysis of orientation of individual functional groups, namely C=O, C-O-C, C-O-O et al., will be presented in our next paper.

MODEL

On the base of the results obtained, one can improve the model of photoorientation described above and uses it to explain the kinetic characteristics. When azo chromophores absorb light and reorient an anisotropic local field appears^[11], which induces reorientation of both side-chain and main-chain fragments as we have seen from IR spectra measurements. In general, one may suppose that, due to mutual interactions of covalently bounded azo dye and main-chain fragments, their spatial distributions tend to be agreed. If irradiation time is short, spatial distribution of main-chain fragments is changed weakly because of their weak mobility. As a result, the photoinduced ordering of the azo dye fragments decreases because of their interaction with the disordered polymer matrix. With the increasing of irradiation time, some degree of main-chain fragments ordering is reached. For this reason, after switching off of irradiation, the parameter of azo dye orientational ordering does not decrease to zero but to some nonzero value which is determined by the partially ordered polymer matrix. Effect of dichroism increasing after switching off irradiation with a long exposure time may be explained by taking into account isomerization of the azo dye chromophores from the *cis*

to *trans* state. As a result, D_{\parallel} increases due to both a greater absorption of *trans* isomers in comparing with *cis* isomers and increasing the parameter of *trans* azo dye fragments ordering.

Now we present the above model in the analytical form. For the save of simplicity, we make some assumptions. First, we suppose that all absorbing fragments are in the ground state of the *trans* or *cis* form, so we can write

$$N = N_{tr} + N_{cis} \quad (1)$$

where N is the concentration of all absorbing fragments, N_{tr} and N_{cis} are concentrations of the azo dye fragments in *trans* and *cis* forms, respectively.

We also suppose that absorption σ_{cis} of a single *cis* isomer is isotropic. Absorption of a *trans* isomer is dichroic with the optical dipole moment directed along its long axis. Let us denote absorption of a *trans* isomer parallel and perpendicular to its long axis as $\sigma_{tr\parallel}$ and $\sigma_{tr\perp}$. Quantum yields of isomerization of *trans* and *cis* isomers under absorption of light are equal to $q_{t \rightarrow c}$ and $q_{c \rightarrow t}$, respectively. We denote distribution function of *trans* isomers as $f(\theta)$, where θ is the angle between the long axis of *trans* isomer and direction of the photoinduced orientation. Let in stationary state, which is reached after switching off irradiating light, the distribution of *trans* isomers be described by a function $\Phi(\theta)$. According to our assumptions, $\Phi(\theta)$ is settled and maintained by the main-chains system ordering.

The kinetics of POA recording and relaxation is defined by three different times:

- 1) life time for *cis* isomers τ_{cis} ;
- 2) relaxation time of the azo dye system τ_s (time of orientational relaxation from $f(\theta)$ to $\Phi(\theta)$);
- 3) ordering time of main-chain system τ_p .

Now one can write down the kinetic equations for angular distributions of *cis* and *trans* isomers and the main-chains fragments. For *cis* isomers, we have:

$$\begin{aligned} \frac{\partial N_{cis}}{\partial t} &= -\sigma_{cis} q_{c \rightarrow t} N_{cis} I - \frac{N_{cis}}{\tau_{cis}} + N_{tr} \int f(\theta) \sigma_{trj} q_{t \rightarrow c} E_i E_j d\Omega \\ &= -\sigma_{cis} q_{c \rightarrow t} N_{cis} I - \frac{N_{cis}}{\tau_{cis}} + N_{tr} I (\sigma_{tr\perp} + \Delta\sigma_{tr} \frac{2}{3} (S + \frac{1}{2})) q_{t \rightarrow c} \end{aligned} \quad (2)$$

where I is the intensity of exciting light, Ω is the solid angle of integrating, which axis coincides with the direction of azo dye alignment, $\Delta\sigma_{tr} = \sigma_{tr\parallel} - \sigma_{tr\perp}$, $S = \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2}$ is the order parameter of *trans* isomers. The first two terms of eq. (2) describe decreasing the number of *cis* isomers due to its transformation into the *trans* form through the excited electron level and activation barrier, respectively. The third term describes increasing the number of *cis* isomers due to the exciting of *trans* isomers.

Angular redistribution of *trans* isomers can be described by the next equation:

$$\begin{aligned} \frac{\partial (N_{tr} f(\theta))}{\partial t} &= \frac{\sigma_{cis} q_{c \rightarrow t} N_{cis} I}{2\pi} + \frac{N_{cis}}{\tau_{cis}} f(\theta) - \sigma_{trj} q_{t \rightarrow c} E_i E_j N_{tr} f(\theta) \\ &\quad - \frac{N_{tr} (f(\theta) - \Phi(\theta))}{\tau_s} \\ &= \frac{\sigma_{cis} q_{c \rightarrow t} N_{cis} I}{2\pi} + \frac{N_{cis}}{\tau_{cis}} f(\theta) - (\sigma_{tr\perp} + \Delta\sigma_{tr} \cos^2 \theta) q_{t \rightarrow c} N_{tr} I f(\theta) \\ &\quad - \frac{N_{tr} (f(\theta) - \Phi(\theta))}{\tau_s} \end{aligned} \quad (3)$$

The first two terms of eq. (3) describe increasing the *trans* isomers concentration due to isomerization of the *cis* form. We regard that new *trans* isomers are redistributed proportionally to the current angular distribution of *trans* isomers $f(\theta)$. The third term describes excitations of *trans* isomers into the *cis* form. The last term accounts decreasing the azo dye ordering due to a disordering action of the polymer matrix.

Finally, the kinetics of main-chains ordering can be simply described in the next way:

$$\frac{\partial \Phi}{\partial t} = - \frac{\Phi(\theta) - f(\theta)}{\tau_p} \quad (4)$$

In general, the system of eqs. (1)-(4) allows us to calculate concentrations of *trans* and *cis* isomers for any direction l at the angle θ with respect to the direction of ordering l_0 , for any time of recording and relaxation of anisotropy. In reality, however, to solve system (1)-(4) is difficult. Therefore, it is more convenient to work with moments of the distribution function $S_{2n} = \int P_{2n}(\cos\theta) f$, where $P_{2n}(\cos\theta)$ are the Legendre polynomials. Then, multiplying eqs. (3) and (4) by $P_{2n}(\cos\theta)$ and integrating over the angle θ , we obtain the infinite system of coupled equations for various moments of the distribution function. For simplicity, we account for only the second moment and then calculate N_{cis} , N_{tr} and S . That allows us to calculate the value of optical density of the sample, the expression for which can be presented in the form:

$$D(\theta) = \sigma_{cis} q_{cis} N_{cis}(\theta) + (\sigma_{tr\perp} + \Delta\sigma_{tr} \cos^2 \theta) q_{tr} N_{tr}(\theta) \quad (5)$$

Experimentally measured values of $D_{||}$ and D_{\perp} are satisfied eq. (5) at $\theta=0^\circ$ and $\theta=90^\circ$, respectively. To calculate the dependences of $D_{||}(t)$ and $D_{\perp}(t)$ with the eqs. (1)-(5) it is necessary to assign values to all input parameters. We do this on the basis of our experimental data and that taken from the literature. On the basis of curve 1 in Fig.3, it is possible to conclude that $\tau_{cis}\tau_t=300$ s. We evaluated the ordering time $\tau_p=900$ s from the slow component of $\Delta n(t)$ in Fig.4, ratio $\sigma_{tr}/\sigma_{tr\perp}=20$ was estimated on the basis of dichroic absorption of the film at $\lambda_{test}=375$ nm (see curves 3 and 3' in Fig.2) taking into account that $S\approx 0.6$ ^[15]. All calculations were performed under the assumption of $\sigma_{cis}\approx\sigma_{tr}$ at $\lambda_{test}=375$ nm. Values for constants $q_{t\rightarrow c}=0.02$ and $q_{c\rightarrow t}=0.6$ were taken from ^[16]. Intensity of exciting light was fitted to experimental data and was equal to 5 mW/cm^2 .

The calculated dependences of $D_{||}(t)$ and $D_{\perp}(t)$ are presented in Fig.5. It is seen that both curves of recording and curves of relaxation are in qualitative agreement with experimental data (Fig.3). For quantitative agreement, more precise measuring of the input parameters in eqs. (1)-(5) is necessary. Note, that the dependences $D_{||}(t)$ and $D_{\perp}(t)$

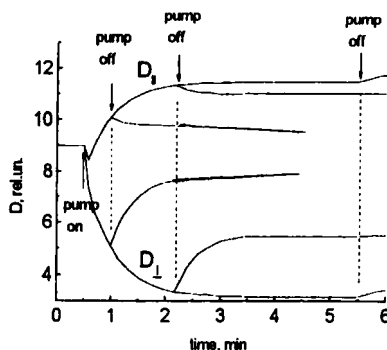


FIGURE 5

contain less information than system (1) - (5). Full solution of eqs. (1)-(5) allows one to calculate the angular distribution of optical density $D(\theta)$ and its evolution through the processes of recording and relaxation.

CONCLUSIONS

Thus, our investigations of anisotropy photoinduction in the azo polymer films give evidence for alignment of both photosensitive azobenzene fragments and non-photosensitive main-chain fragments. We think that main-chains are aligned with strong anisotropic local field produced by highly light oriented azobenzene chromophores. On the other hand, the alignment of main-chains stabilizes the orientation of azobenzene fragments after switching off the exciting light. Taking into account these processes, it is possible to conform the calculation of kinetic curves with experimental data. We believe that mechanisms of photoorientation described here are suitable one for dichroic dyes containing polymers.

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