

Spatial reorientation of azobenzene side groups of a liquid crystalline polymer induced by linearly polarized light

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Abstract. The photoinduced 3D orientational structures in films of a liquid crystalline polyester, containing azobenzene side groups, are studied both experimentally and theoretically. By using the null ellipsometry and the UV/Vis absorption spectroscopy, the preferential in-plane alignment of the azobenzene fragments and in-plane reorientation under irradiation with linearly polarized UV light are established. The uniaxial and biaxial orientational order of the azobenzene chromophores are detected. The biaxiality is observed in the intermediate stages of irradiation, whereas the uniaxial structure is maintained in the photosaturated state of the photo-orientation process. The components of the order parameter tensor of the azobenzene fragments are estimated for the initial state and after different doses of irradiation. The proposed theory takes into account biaxiality of the induced structures. Numerical analysis of the master equations for the order parameter tensor is found to yield the results that are in good agreement with the experimental dependencies of the order parameter components on the illumination time.

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1 Introduction

The effect of photoinduced optical anisotropy (POA) is an ability of some photosensitive materials to become dichroic and birefringent under the action of light. The capability of having the light-controlled anisotropy makes the materials that exhibit POA very promising and highly perspective for use in many photonic applications such as optical data storage and processing, telecommunication and reversible holography [1,2]. In addition, it was found that substances with POA effect serve as excellent aligning substrates for liquid crystals [3,4].

Polymers containing covalently linked photochromic moieties such as azobenzene derivatives are known as azopolymers. These materials exhibit POA of extremely high efficiency: the value of photoinduced birefringence in azopolymers can be as high as 0.3 and the dichroic ratio of the absorption is over 10. This makes azopolymers particularly suitable for the investigation of light-induced ordering processes. This is why in the last decade these polymers have been the subject of intense experimental and theoretical studies [2,5–12].

The accepted mechanism of POA induced by the linearly polarized UV light involves induced *trans-cis*-photoisomerization and subsequent thermal and/or photochemical *cis-trans*-back-isomerization of the azobenzene moieties. Since the optical dipole of $\pi\pi^*$ and of the $n\pi^*$ transition of the azobenzene moiety is directed along its long molecular axis, the fragments oriented perpendicular to the actinic light polarization vector, \mathbf{E} , then become almost inactive, whereas the others with suitable orientation are active undergoing photoisomerization. These *trans-cis-trans* photoisomerization cycles are accompanied by rotations of the azobenzene chromophores resulting eventually in an orientation of the long axes of the azobenzene fragments along all directions normal to the polarization vector of the incident actinic light. Non-photoactive groups then undergo reorientation due to co-operative motion or dipole interaction [10–14].

The above scenario, known as photo-orientation mechanism, assumes angular redistribution of the long axes of the *trans* molecules during the *trans-cis-trans* isomerization cycles. It was initially suggested in [15], for the case when the *cis* state has a short lifetime, that it becomes temporarily populated during this process but reacts immediately back to thermodynamically stable *trans* isomeric form.

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Another limiting case is known as the angular selective hole burning mechanism (photoselection) and occurs when the *cis* states are long living. In this case POA is caused by the selective depletion of the *trans* isomeric form during the establishment of the steady state [7]. The anisotropy induced in this way is not long-term stable and disappears as a result of the thermal back reaction. The photo-orientation process in the steady state of the photoisomerization takes place simultaneously, but it needs longer time to saturate. Generally, both mechanisms contribute to POA.

It is evident from the foregoing that the actinic light results in the orientation of azobenzene chromophores perpendicular to the polarization vector **E**. These directions can be thought of as equivalent provided that the symmetry group of the system includes rotations. From the experimental results, however, the latter is not the case. In particular, it was found that the photoinduced orientational structures can show biaxiality [6,16–18]. The variety of orientational configurations (uniaxial, biaxial, splayed) with different spatial orientations of the principle axes can be expected depending on many factors such as chemical structure of polymer, method of film preparation, irradiation conditions and so on.

In the past years this spatial character of the photo-orientation has not received much attention. It was neglected in the bulk of experimental and theoretical studies of POA in azobenzene containing polymers [2,5,10,7–9,11]. One conceivable reason for this can be the lack of appropriate experimental methods. On the other hand, until recently, the problems related to the 3D orientational structures in polymeric films has not been of major interest for applications. But such kind of studies are currently of considerable importance in the development of new compensation films for liquid crystal (LC) displays [19] and the pretilt angle generation by the use of the photoalignment method of LC orientation [20].

The known methods suitable for the experimental study of the 3D orientational distributions in polymer films can be divided into two groups.

The methods of the first group are based on absorption measurements. These methods have the indisputable advantage that the order parameters of various molecular groups can be estimated from the results of these measurements. Shortcomings of the known absorption methods [6,21] are the limited field of applications and the strong approximations.

The second group includes the methods dealing with principle refractive indices. Recently, several variations of the prism coupling methods have been applied to measure the principle refractive indices in azopolymer films [22–24]. These results, however, were not used for an in-depth analysis of such features of the spatial ordering as biaxiality and spatial orientation of the optical axes depending on polymer chemical structure, irradiation conditions, etc.

Our goal is a comprehensive investigation of the peculiarities of 3D orientational ordering in azopolymers. The present work is a part of a study focused on the

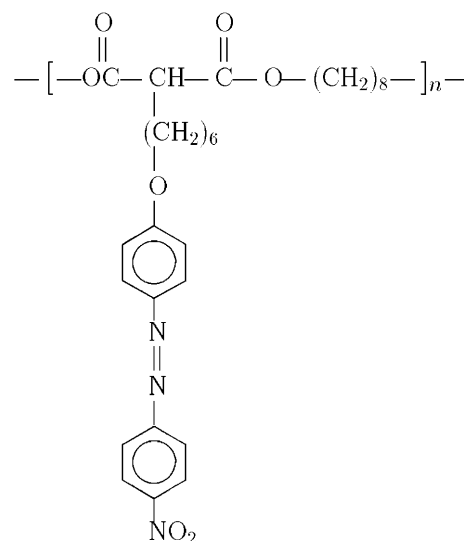


Fig. 1. Structural formula of the azopolymer.

orientational biaxiality and the transition from biaxial to uniaxial structures caused by the polarized actinic light.

The paper is organized as follows.

In Section 2 we describe our combined approach based on using the methods that deal with both absorption and birefringence measurements. The modified null ellipsometry method is employed to study the general structure of the anisotropic polymer films. The components of order parameter tensor of the azobenzene chromophores are estimated from the results of the UV absorption measurements.

Material of Section 3 comprises the theoretical part of the paper. We begin with the analysis of the general kinetic rate equations and show how the known results [9,11] can be recovered by using our theoretical approach. Then we formulate the phenomenological model of the photoinduced ordering in azopolymers that accounts for biaxiality of the induced structures and long-term stability of POA. After computing the order parameter components of azobenzene units for different irradiation doses, we find that the predictions of the theory are in good agreement with the data obtained experimentally.

Finally in Section 4 we draw the results and make some concluding remarks.

2 Experimental

2.1 Samples preparation and irradiation procedure

We investigated POA using poly[octyl(4-hexyloxy-4'-nitro)azobenzenemalonate] (the structural formula is given in Fig. 1) as model polymer whose synthesis is described in [25]. The thermal properties of the polymer are characterized by the transition temperatures C_1 -32°- C_2 -44°-S 52°-N-55°-I detected by DSC and polarizing microscopy of the polymer in the bulk. (The two crystalline states are labelled C_1 and C_2 ; the symbols S

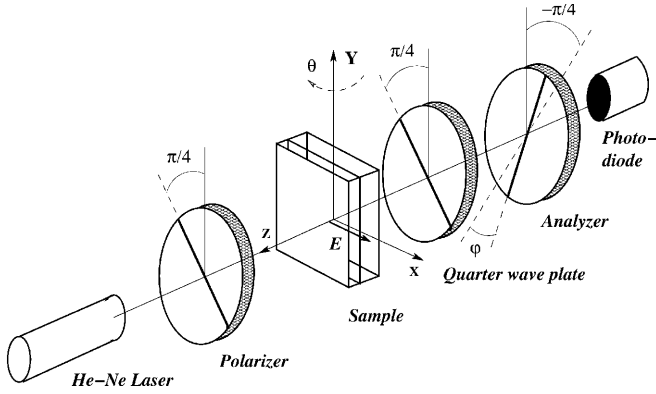


Fig. 2. Experimental setup for the null ellipsometry measurements.

and N stand for nematic and smectic mesophases, respectively; the symbol I corresponds to the isotropic melt.) The polymer was solved in dichloroethane and spin-coated on the quartz slabs. The prepared films were kept at a room temperature for 24 h for the evaporation of the solvent. The thickness of the films of about 200–600 nm was measured with a profilometer of Tencor Instruments.

In order to induce anisotropy in the films, we used the irradiation of a Hg lamp in combination with an interference filter (365 nm). The intensity of the actinic light was about 1.0 mW/cm^2 . A Glan-Thompson polarizer was applied for the polarization of the UV light. A normal incidence of the actinic light was used in our studies.

The irradiation was provided in several steps followed by both birefringence and absorption measurements. In order to have ordering processes in the films completed after switching off the irradiation, the waiting time interval before the measurements was longer than 15 min. According to [12], it corresponds to a time period which guarantees that all *cis* isomers react back to the *trans* form.

2.2 Null ellipsometry method

Instead of the prism coupling methods commonly used for the estimation of principle refractive indices, we applied null ellipsometry technique [26] dealing with birefringence components. By this means we have avoided some disadvantages of the prism coupling method such as the problem of making optical contact between the prism and the polymer layer.

The optical scheme of our method is presented in Figure 2. The polymer film is placed between the crossed polarizer and the analyzer and a quarter wave plate with the optic axes oriented parallel to the polarization direction of the polarizer. The light beam, whose wavelength is far away from the absorption band of the polymer, is passing through the optical system. The elliptically polarized beam passing through the sample is transformed into the linearly polarized light by means of the quarter wave plate. The polarization plane of this light is turned with respect to the polarization direction of the polarizer. This rotation is related to the phase retardation acquired

by the light beam after passing through the film under investigation. It can be compensated by rotating the analyzer by the angle ϕ that encodes information on the phase retardation.

This method used for the normal incidence of the testing light is known as the Senarmont technique. It is suitable for the in-plane birefringence measurements.

Using oblique incidence of the testing beam we have extended this method for estimation of both in-plane, $n_y - n_x$, and out-of-plane $n_z - n_x$ birefringence (n_x , n_y and n_z are the principle refractive indices of the film shown in Fig. 2). In this case, the angle ϕ depends on the in-plane retardation $(n_y - n_x)d$, the out-of-plane retardation $(n_z - n_x)d$ and the absolute value of a refractive index of the biaxial film, say, n_x .

We need to have the light coming out of the quarter wave plate almost linearly polarized when the system analyzes the phase shift between two orthogonal eigenmodes of the sample. In our experimental setup this requirement can be met when the x -axis, directed along the polarization vector of the actinic light, is oriented horizontally or vertically. Dependencies of the analyzer rotation angle ϕ on the incidence angle of the testing beam θ were measured for both the vertical and horizontal orientation of the x -axis. The value of n_x was measured with the Abbe refractometer independently.

By using Berreman's 4×4 matrix method [27], the θ -dependencies of ϕ were calculated. Maxwell's equations for light propagation through the system of polarizer, sample and quarter wave plate were solved numerically for the different configurations of optical axes in the samples. The measured and computed ϕ versus θ curves were fitted in the most probable configuration model using the measured value of n_x .

We conclude on the alignment of the azobenzene fragments from the obtained values of $(n_y - n_x)d$ and $(n_z - n_x)d$ assuming that the preferred direction of these fragments coincides with the direction of the largest refractive index. More details on the method can be found in our previous publication [18].

In our setup designed for the null ellipsometry measurements we used a low-power He-Ne laser ($\lambda = 632.8 \text{ nm}$), two Glan-Thompson polarizers mounted on rotational stages from Oriel Corp., a quarter wave plate from Edmund Scientific and a sample holder mounted on the rotational stage. The light intensity was measured with a photodiode. The setup was automatically controlled by a personal computer. The rotation accuracy of the analyzer was better than 0.2 degrees.

2.3 Absorption measurements

The UV/Vis absorption measurements were carried out using a diode array spectrometer (Polytec XDAP V2.3). The samples were set normally to the testing beam of a deuterium lamp. A Glan-Thompson prism with a computer-driven stepper was used for the polarization of the testing beam. The UV spectra of the original as well as of the irradiated films were measured in the spectral

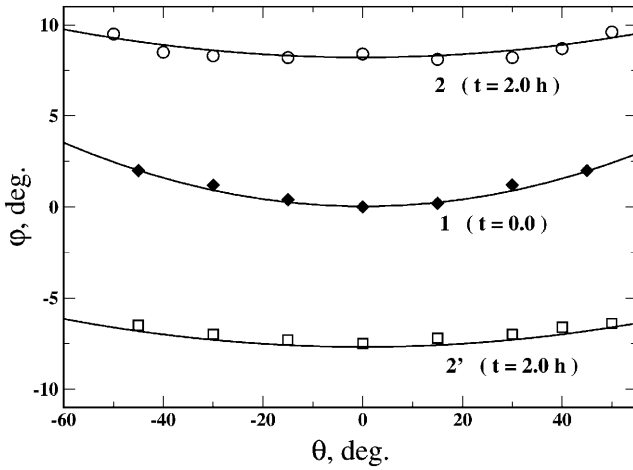


Fig. 3. Dependencies of the phase shift ϕ on the incidence angle θ measured before (curve 1) and after irradiation (curves 2 and 2'). The curves 2 and 2' correspond to horizontal and vertical orientations of the x -axis, respectively.

range of 220–400 nm with a rotation step of the polarizer of 5 degrees.

From these measurements the optical density components corresponding to the absorption maximum of azobenzene chromophores were estimated for the polarization direction of the testing light parallel to the x and y axes, respectively. We denote them as D_x and D_y , respectively. The out-of-plane component, D_z , was estimated by making use of the method proposed in [6,28]. The latter assumes that the sample has a uniaxial structure with in-plane position of the axis of anisotropy at the instant of time t_0 . It implies that $D_z(t_0) = D_x(t_0)$ and the total absorption can be estimated as follows:

$$D_{\text{total}} = D_x(t_0) + D_y(t_0) + D_z(t_0) = 2D_x(t_0) + D_y(t_0). \quad (1)$$

When the number of *trans* azobenzene units does not change considerably, the total absorption is constant and the value of D_z at the instant of time t can be determined from the following equation:

$$D_z(t) = D_{\text{total}} - D_x(t) - D_y(t), \quad (2)$$

where $D_x(t)$ and $D_y(t)$ are the experimentally measured parameters.

2.4 Experimental results

Curve 1 in Figure 3 shows the phase shift ϕ versus the incidence angle θ curve measured with the null ellipsometry method for the non-irradiated polymer film. The curves $\phi(\theta)$ measured for the vertical and horizontal position of the x -axis overlap. In addition, it is seen that there is no phase shift for normal light incidence ($\theta = 0$). So we arrive at the conclusion that the in-plane indices are matched: $n_y = n_x$. The film, however, possesses out-of-plane birefringence $(n_z - n_x)d = -20$ nm that results in a phase shift at oblique light incidence.

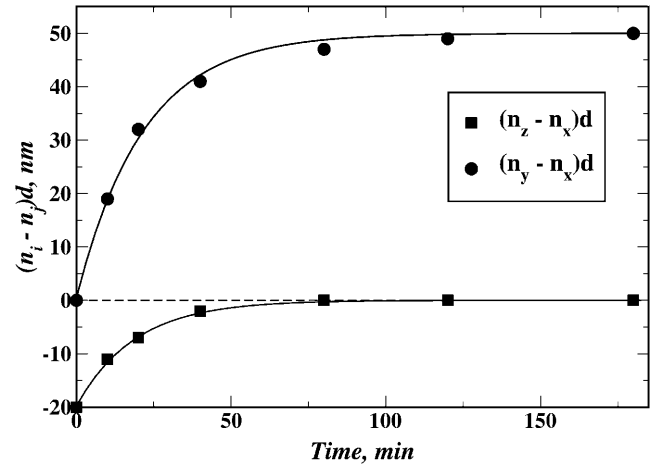


Fig. 4. In-plane and out-of-plane birefringence as a function of the irradiation time.

The fitting gives the following relations for the principal refractive indices: $n_z < n_x = n_y$ and $n_z - n_x \approx -0.1$. The film, therefore, shows a negative birefringence with the optical axis normal to the film surface. The relationship between the three indices suggests that the azobenzene fragments are randomly distributed in the plane of the film with no preferred direction for their orientation (a degenerate in-plane distribution).

The ϕ versus θ dependencies measured after 2 h of UV light irradiation are shown in Figure 3. These curves correspond to the horizontal (curve 2) and vertical (curve 2') positions of the film x -axis.

According to the modeling, a positive phase shift corresponds to the axis in the horizontal direction having the higher in-plane refractive index n_y perpendicular to the UV light polarization and the lower in-plane index n_x . From the curve fitting we have $n_y - n_x = 0.25$ ($(n_y - n_x)d \approx 50$ nm), $(n_z - n_x)d = 0$ nm, $n_y > n_x = n_z$. The light-induced structure is positive uniaxial with the optical axis perpendicular to the UV light polarization. In this case, the azobenzene fragments show an in-plane alignment perpendicular to the UV light polarization.

The fitted values of the in-plane, $n_y - n_x$, and out-of-plane birefringence, $n_z - n_x$, for various irradiation times are presented in Figure 4. For small irradiation doses the principal refractive indices are different: $n_z < n_x < n_y$. The in-plane birefringence monotonously increases up to a saturated value with the increase of irradiation time. On the other hand, the difference between n_x and n_z decreases and becomes negligible in the photosaturated state. So the film is biaxial at the intermediate stages of irradiation, whereas the photosaturated state can be characterized as a uniaxial structure. The optical axis of this structure lies in the plane of the film and is directed along the y -axis.

The null ellipsometry identifies a general orientational structure, but it does not provide the means to estimate the order parameters of various molecular groups. Different absorption methods are common for this purpose. In this case the wavelength of the testing light is tuned to the absorption maximum of the selected molecular fragments.

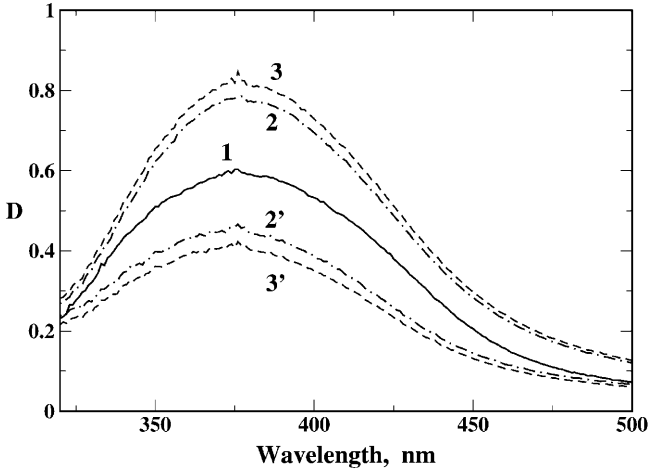


Fig. 5. UV absorption spectra measured before (curve 1) and immediately after the irradiation with UV light linearly polarized in the x direction over 1 h (curves 2 and 2'). The stationary spectra D_y and D_x (the waiting time is 15 min) are shown as curves 3 and 3', respectively.

In order to estimate the order parameter of azobenzene units, we carried out UV absorption measurements in the absorption maximum of azobenzene chromophores. The UV/Vis spectrum of the studied azopolymer is presented in Figure 5 (curve 1). It contains the intensive absorption band with a maximum at $\lambda = 377$ nm corresponding to the $\pi\pi^*$ transition of *trans* azobenzene fragments.

The spectrum reveals polarization splitting during irradiation with polarized light. The polarization components D_y and D_x , measured just after switching off the actinic light, are depicted in Figure 5 as 2 and 2', respectively. These spectra show changes that become stationary for approximately 10 min.

The stationary spectra D_y and D_x are shown in Figure 5 as curves 3 and 3', respectively. In order to have the azobenzene units relaxed to the stationary state, the components D_x and D_y were measured 15 min after each irradiation period.

The experimentally measured absorption components D_x and D_y before irradiation and for different irradiation doses are presented in Figure 6a. The kinetics of D_x and D_y is typical of the reorientation mechanism of azobenzene units [7]. Both curves reveal saturation. As was shown by the null ellipsometry method, the saturated state of the polymer film under consideration is uniaxial with the in-plane orientation of the anisotropy axis.

In order to prove that the method described in Section 2.3 can be applied to estimate D_z , we need to show that, as compared to the non-irradiated film, the number of *trans* isomers does not change in the state relaxed after the irradiation. This is the case when the lifetime of *cis* isomers is shorter than the time of the spectral relaxation after switching off the actinic light.

In order to estimate the lifetime of *cis* isomers we have measured the relaxation of the spectral changes at $\lambda_t = 377$ nm after irradiation with non-polarized light. Incidence directions of both actinic and testing light were

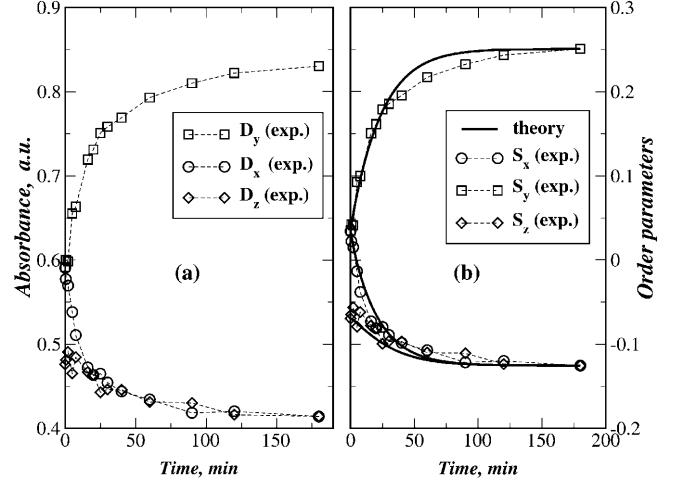


Fig. 6. Dependencies of (a) the principal absorption coefficients and (b) the order parameter components on the irradiation time. Theoretical curves for the diagonal components of the order parameter tensor are shown as solid lines.

approximately normal to the film. It was found that the relaxation curve $D(t)$ contains two components with characteristic times of 1.0 s and 4 min, respectively. The first value can be attributed to a *cis-trans* transition of azobenzene chromophores. The other time can be related to either the small fraction of long-living *cis* isomers or more likely to the orientational relaxation of the azobenzene units. In any case, the waiting time of 15 min ensures that we definitely have all the *cis* isomers transformed into the *trans* form.

So in our measurements the concentration of *trans* isomers is preserved and the method described in Section 2.3 can be applied. The values of D_z calculated for various irradiation doses using equations (1-2) are presented in Figure 6a. Dependencies $D_x(t)$, $D_y(t)$ and $D_z(t)$ show that the photoinduced ordering is mainly due to the in-plane reorientation of azobenzene fragments in the y direction. In addition, a slight reorientation in the z direction is observed.

The orientational structure is generally described by the tensor S_{ij} , which is diagonal when the co-ordinate axes are directed along the principal axes of the film. The diagonal elements $S_{xx} \equiv S_x$, $S_{yy} \equiv S_y$ and $S_{zz} \equiv S_z$ are related to the absorption components D_x , D_y and D_z [6]. For example,

$$S_x = \frac{2D_x - (D_y + D_z)}{2(D_x + D_y + D_z)}. \quad (3)$$

The components S_y and S_z can be obtained by the cyclic permutation in expression (3).

The values of S_x , S_y and S_z calculated using equation (3) are presented in Figure 6b. As is seen, during the initial stage of irradiation, the orientational configuration is biaxial, whereas the initial and the photosaturated states are uniaxial. These structures are characterized by the following order parameters: $S_x = S_y \approx 0.035$ and $S_z \approx$

−0.07 for the non-irradiated film; $S_x = S_z \approx -0.1255$ and $S_y \approx 0.251$ for the film in the photosaturated state.

The transition between biaxial and uniaxial photoinduced orientations will be the subject of subsequent studies. We believe that a tendency to form a uniaxial structure is related to the intrinsic property of self-organization of mesogenic groups. Theoretically, a similar tendency of nematic liquid crystals can be related to some specific features of the phase transition reflected in the form of the mean-field free energy [29]. In this connection we assume that the irradiation with polarized light causes both the photo-orientation of azochromophores and the self-aggregation, as was found for other liquid crystalline azopolymers [30,31].

3 Theory

Before we proceed with theoretical considerations, let us emphasize the following distinguishing features of POA in liquid crystalline azopolymers:

- (a) in contrast with the reversible POA, considered in [32–35,15], where POA disappears after switching off the irradiation, POA in liquid crystalline azopolymers can only be thermally erased by heating above clearing temperature. The long-term stability of POA is caused by the photo-orientation of the azobenzene;
- (b) the biaxiality effects discussed in Section 1.

Clearly, we can conclude that the photo-orientation is a non-equilibrium process in a rather complex polymer system and it still remains a challenge to develop a tractable theory treating all the above points adequately.

As far as the long-term stability of POA is concerned, the reorientation of the azobenzene groups can be assumed to result in the appearance of a self-consistent anisotropic field that supports induced anisotropy. This field comes from anisotropic interactions between the azobenzene fragments and rearrangement of the main chains and other non-absorbing fragments. In other words, the photoinduced orientational structures can be regarded as a result of the photo-reorientation and thermotropic self-organization processes [30].

There are two phenomenological models based on similar assumptions: the multidomain model proposed in [9] and the model with additional order parameter, attributed to the polymer backbone and introduced to make the steady state degenerate [11].

Despite the fact that these models look different, it is clear that they incorporate the long-term stability by introducing an additional degree of freedom (subsystem) whose kinetics would reflect co-operative motion and account for non-equilibrium behavior.

In this section we describe our theoretical approach to the kinetics of the photoinduced reorientation. We begin with the analysis of general master equations and specialize then the rates of the involved transitions. The resulting kinetic equations for order parameters are derived after making assumptions on the form of the angular redistribution probabilities and the order parameter correlation

functions. In addition, we show that this approach can be employed to derive the known phenomenological models [9,11,12]. Finally, at the end of the section we present the numerical results obtained by solving the kinetic equations for the order parameters and concentrations.

3.1 Master equations

We shall assume that the dye molecules in the ground state are of *trans* form with the orientation of the molecular axis defined by the unit vector $\hat{\mathbf{n}}$. The latter is specified by the polar, θ , and azimuthal, ϕ , angles: $\hat{\mathbf{n}} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$.

The angular distribution of the *trans* molecules at time t is characterized by the number distribution function $N_{tr}(\hat{\mathbf{n}}, t)$. Molecules in the excited state have the *cis* conformation and the corresponding function is $N_{cis}(\hat{\mathbf{n}}, t)$. Then for the number of *trans* and *cis* molecules we have

$$N_{tr}(t) \equiv N n_{tr}(t) = \int N_{tr}(\hat{\mathbf{n}}, t) d\hat{\mathbf{n}}, \quad (4)$$

$$N_{cis}(t) \equiv N n_{cis}(t) = \int N_{cis}(\hat{\mathbf{n}}, t) d\hat{\mathbf{n}}, \quad (5)$$

$$N = N_{tr}(t) + N_{cis}(t), \quad n_{tr}(t) + n_{cis}(t) = 1, \quad (6)$$

where $\int d\hat{\mathbf{n}} \equiv \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta$, and N is the total number of molecules.

We shall refer to the additional subsystem that is able to accumulate induced ordering of the side chain molecules as a polymer system (matrix). From the phenomenological point of view, this system can be thought to represent some collective degrees of freedom of non-absorbing units such as main chains. We shall suppose that it is characterized by the angular distribution function $f_p(\hat{\mathbf{n}}, t)$, so that $N_p(\hat{\mathbf{n}}, t) = N_p f_p(\hat{\mathbf{n}}, t)$. Note that the coefficient N_p can be considered as an effective number of the units related to the polymer system. But, to be more precise, we will show that this factor determines the relations between different thermal relaxation constants (see Eq. (14)).

The starting point of our approach is the kinetic rate equations taken in the following general form [36,37]:

$$\begin{aligned} \frac{\partial N_\alpha}{\partial t} = & \left[\frac{dN_\alpha}{dt} \right]_{\text{Diff}} + \sum_{\beta \neq \alpha} \int \left[W(\alpha, \hat{\mathbf{n}} | \beta, \hat{\mathbf{n}}') N_\beta(\hat{\mathbf{n}}', t) - \right. \\ & \left. - W(\beta, \hat{\mathbf{n}}' | \alpha, \hat{\mathbf{n}}) N_\alpha(\hat{\mathbf{n}}, t) \right] d\hat{\mathbf{n}}', \end{aligned} \quad (7)$$

where $\alpha, \beta \in \{tr, cis, p\}$.

The first term on the right-hand side of equation (7) is due to the rotational diffusion of molecules in *trans* ($\alpha = tr$) and *cis* ($\alpha = cis$) conformations. Note that the terms proportional to $W(\alpha, \hat{\mathbf{n}} | \alpha, \hat{\mathbf{n}}')$ can be incorporated into this diffusion term. In what follows it is supposed that

$$\left[\frac{dN_{tr}}{dt} \right]_{\text{Diff}} = \left[\frac{df_p}{dt} \right]_{\text{Diff}} = 0. \quad (8)$$

Now in order to proceed we need to specify the rates of the transitions.

3.2 Transition rates

The *trans* \rightarrow *cis* transition is stimulated by the incident UV light quasisresonant to the transition. Assuming that the electromagnetic wave is linearly polarized along the *x*-axis, the transition rate can be written as follows [33, 35]:

$$W(cis, \hat{\mathbf{n}} | tr, \hat{\mathbf{n}}') = \Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') P_{tr}(\hat{\mathbf{n}}'),$$

$$\int \Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') d\hat{\mathbf{n}} = 1, \quad (9)$$

$$P_{tr}(\hat{\mathbf{n}}') = (\hbar\omega_t)^{-1} \Phi_{tr \rightarrow cis} \sum_{i,j} \sigma_{ij}^{(tr)}(\hat{\mathbf{n}}') E_i E_j^* =$$

$$= q_t I (1 + u n_x^2) \equiv q_t I (1 + u (2S_x + 1)/3), \quad (10)$$

where $\sigma^{(tr)}(\hat{\mathbf{n}})$ is the tensor of absorption cross-section for the *trans* molecule oriented along $\hat{\mathbf{n}}$: $\sigma_{ij}^{(tr)} = \sigma_{\perp}^{(tr)} \delta_{ij} + (\sigma_{\parallel}^{(tr)} - \sigma_{\perp}^{(tr)}) n_i n_j$; $u \equiv (\sigma_{\parallel}^{(tr)} - \sigma_{\perp}^{(tr)})/\sigma_{\perp}^{(tr)}$ is the absorption anisotropy parameter; $\hbar\omega_t$ is the photon energy; $\Phi_{tr \rightarrow cis}$ is the quantum yield of the process and $\Gamma_{tr}(\hat{\mathbf{n}}, \hat{\mathbf{n}}')$ describes the angular redistribution of the molecules excited in the *cis* state; I is the pumping intensity.

A similar line of reasoning applies to the *cis* \rightarrow *trans* transition, so we have

$$W(tr, \hat{\mathbf{n}} | cis, \hat{\mathbf{n}}') = \gamma_c \Gamma_{c-t}^{(sp)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') + q_c I \Gamma_{c-t}^{(ind)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}'),$$

$$q_c \equiv \Phi_{cis \rightarrow trans} \sigma^{(cis)}, \quad (11)$$

where $\gamma_c \equiv 1/\tau_c$, τ_c is the lifetime of *cis* molecule and the anisotropic part of the absorption cross-section is disregarded, $\sigma_{\parallel}^{(cis)} = \sigma_{\perp}^{(cis)} \equiv \sigma^{(cis)}$. Equation (11) implies that the process of angular redistribution for induced and spontaneous transitions can differ. Note that the normalization condition for all the angular redistribution probability intensities is

$$\int \Gamma_{\beta-\alpha}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') d\hat{\mathbf{n}} = 1. \quad (12)$$

The remaining part of the transitions describes the process that equilibrates the side chain absorbing molecules and the polymer system. The corresponding rates can be taken in the form

$$W(\alpha, \hat{\mathbf{n}} | p, \hat{\mathbf{n}}') = \gamma_{p-\alpha} \Gamma_{p-\alpha}(\hat{\mathbf{n}}, \hat{\mathbf{n}}'),$$

$$W(p, \hat{\mathbf{n}} | \alpha, \hat{\mathbf{n}}') = \gamma_{\alpha-p} \Gamma_{\alpha-p}(\hat{\mathbf{n}}, \hat{\mathbf{n}}'), \quad \alpha \in \{tr, cis\}, \quad (13)$$

where $\gamma_{p-\alpha}$ and $\gamma_{\alpha-p}$ are angular independent. In addition, since thermal relaxation does not change the number of molecules in a particular state, we have the relation for $\gamma_{p-\alpha}$ and $\gamma_{\alpha-p}$:

$$N_p \gamma_{p-\alpha} = N n_{\alpha} \gamma_{\alpha-p}. \quad (14)$$

As was mentioned above, this equation relates the thermal relaxation constants of the polymer and the fragments through the coefficient N_p , introduced in Section 3.1.

3.3 Model

At this stage it is convenient to introduce the normalized angular distribution functions, $f_{\alpha}(\hat{\mathbf{n}}, t)$:

$$N_{\alpha}(\hat{\mathbf{n}}, t) = N n_{\alpha}(t) f_{\alpha}(\hat{\mathbf{n}}, t). \quad (15)$$

From equations (7, 9) and (11) it is not difficult to obtain the equation for $n_{tr}(t)$:

$$\frac{\partial n_{tr}(t)}{\partial t} = (\gamma_c + q_c I) n_{cis}(t) - \langle P_{tr} \rangle_{tr} n_{tr}(t), \quad (16)$$

where the angular brackets $\langle \dots \rangle_{\alpha}$ stand for averaging over angles with the distribution function f_{α} . Owing to condition (12), this equation does not depend on the form of the angular redistribution probabilities.

From the results of the previous section and equation (16), we derive the equations for the distribution functions

$$n_{cis}(t) \frac{\partial f_{cis}(\hat{\mathbf{n}}, t)}{\partial t} = n_{cis}(t) \left\{ \left[\frac{df_{cis}}{dt} \right]_{\text{Diff}} - \gamma_{cis} f_{cis}(\hat{\mathbf{n}}, t) \right\} - \langle P_{tr} \rangle_{tr} n_{tr}(t) f_{cis}(\hat{\mathbf{n}}, t)$$

$$+ n_{tr}(t) \int \Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') P_{tr}(\hat{\mathbf{n}}') f_{tr}(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}'$$

$$+ \gamma_{cis} n_{cis}(t) \int \Gamma_{p-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_p(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}', \quad (17)$$

$$n_{tr}(t) \frac{\partial f_{tr}(\hat{\mathbf{n}}, t)}{\partial t} = -n_{tr}(t) [P_{tr}(\hat{\mathbf{n}}) - \langle P_{tr} \rangle_{tr} + \gamma_{tr}] f_{tr}(\hat{\mathbf{n}}, t)$$

$$+ \gamma_c n_{cis}(t) \int \Gamma_{c-t}^{(sp)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_{cis}(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}'$$

$$+ q_c I n_{cis}(t) \int \Gamma_{c-t}^{(ind)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_{cis}(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}'$$

$$- (\gamma_c + q_c I) n_{cis}(t) f_{tr}(\hat{\mathbf{n}}, t)$$

$$+ \gamma_{tr} n_{tr}(t) \int \Gamma_{p-t}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_p(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}', \quad (18)$$

$$\frac{\partial f_p(\hat{\mathbf{n}}, t)}{\partial t} = -\gamma_p^{(tr)} n_{tr}(t) \left(f_p(\hat{\mathbf{n}}, t) - \int \Gamma_{t-p}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_{tr}(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}' \right) - \gamma_p^{(cis)} n_{cis}(t) \left(f_p(\hat{\mathbf{n}}, t) - \int \Gamma_{c-p}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_{cis}(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}' \right), \quad (19)$$

where $\gamma_{tr} \equiv \gamma_{tr-p}$, $\gamma_{cis} \equiv \gamma_{cis-p}$ and $\gamma_p^{(\alpha)} \equiv N \gamma_{\alpha}/N_p$. Equations (16-19) are derived on the basis of rather general considerations. They can be regarded as a starting

point for the formulation of a number of phenomenological models. We can now describe our model.

Our basic assumptions on the angular redistribution operators $\Gamma_{\alpha-\beta}$ are as follows:

$$\begin{aligned} \gamma_{cis} = 0, \quad \Gamma_{c-t}^{(sp)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') &= \Gamma_{p-t}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \\ &= \Gamma_{t-p}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \delta(\hat{\mathbf{n}} - \hat{\mathbf{n}}'), \end{aligned} \quad (20)$$

$$\Gamma_{c-t}^{(ind)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = f_{tr}(\hat{\mathbf{n}}, t), \quad \Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = f_{cis}(\hat{\mathbf{n}}, t). \quad (21)$$

This gives the resulting system of kinetic equations:

$$\frac{\partial f_{cis}}{\partial t} = \left[\frac{df_{cis}}{dt} \right]_{\text{Diff}}, \quad (22a)$$

$$\begin{aligned} n_{tr} \frac{\partial f_{tr}}{\partial t} &= (\langle P_{tr} \rangle_{tr} - P_{tr}) n_{tr} f_{tr} \\ &+ \gamma_c n_{cis} (f_{cis} - f_{tr}) + \gamma_{tr} n_{tr} (f_p - f_{tr}), \end{aligned} \quad (22b)$$

$$\frac{\partial f_p}{\partial t} = \gamma_p n_{tr} (f_{tr} - f_p), \quad (22c)$$

where $\gamma_p \equiv \gamma_p^{(tr)}$.

Clearly, the meaning of equation (20) is that the molecules do not change the orientation under spontaneous transitions. On the other hand, from equation (21), projecting onto the angular distribution function of the corresponding state describes the angular redistribution for the stimulated transitions.

In order to explain the meaning of the projectors, note that the multidomain model considered in [9] can be derived from equations (17-19) by putting $\gamma_c = 0$, $\gamma_{cis} = \gamma_{tr}$ and assuming that all angular redistribution probabilities are equal to the equilibrium distribution, $\Gamma_{\alpha-\beta}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = p(\hat{\mathbf{n}})$, determined by the mean-field potential $W(\hat{\mathbf{n}})$: $p(\hat{\mathbf{n}}) \propto \exp(-W)$. In other words, this procedure introduces the mean-field potential by assuming that the angular redistribution operators $\Gamma_{\alpha-\beta}$ act as projectors onto the equilibrium distribution. Note that the results of [11, 12] correspond to the case where $\Gamma_{c-t}^{(sp)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = f_{tr}(\hat{\mathbf{n}}, t)$ and $\Gamma_{c-t}^{(ind)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = (4\pi)^{-1}$.

3.4 Order parameters

We can now deduce the equations that describe the temporal evolution of the diagonal components of the order parameter tensor

$$\mathbf{S}(\hat{\mathbf{n}}) = 2^{-1} (3n_i n_j - \delta_{ij}) \hat{\mathbf{e}}_i \otimes \hat{\mathbf{e}}_j. \quad (23)$$

The components of interest can be expressed in terms of Wigner D -functions [38] as follows:

$$\begin{aligned} S_x &\equiv S_{xx}(\hat{\mathbf{n}}) = (3n_x^2 - 1)/2 = \\ &= -(D_{00}^2(\hat{\mathbf{n}}) - \sqrt{6} \text{Re } D_{20}^2(\hat{\mathbf{n}}))/2, \end{aligned} \quad (24)$$

$$\begin{aligned} S_y &\equiv S_{yy}(\hat{\mathbf{n}}) = (3n_y^2 - 1)/2 = \\ &= -(D_{00}^2(\hat{\mathbf{n}}) + \sqrt{6} \text{Re } D_{20}^2(\hat{\mathbf{n}}))/2, \end{aligned} \quad (25)$$

$$S_z \equiv S_{zz}(\hat{\mathbf{n}}) = (3n_z^2 - 1)/2 = D_{00}^2(\hat{\mathbf{n}}). \quad (26)$$

The simplest case occurs for the order parameters of *cis* molecules. Integrating equation (22a) multiplied by $S_{ij}(\hat{\mathbf{n}})$ over angles gives the following result:

$$\frac{\partial S_{ij}^{(cis)}}{\partial t} = -6D_r S_{ij}^{(cis)}, \quad (27)$$

where $S_{ij}^{(\alpha)} \equiv \langle S_{ij}(\hat{\mathbf{n}}) \rangle_\alpha$ and D_r is the rotational diffusion constant. Clearly, our assumptions, $\Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = f_{cis}(\hat{\mathbf{n}}, t)$ and $\gamma_{cis} = 0$, correspond to the case where the presence of *cis* molecules is of minor importance for the ordering kinetics.

Similarly, we can now multiply equations (22b) and (22c) by $S_{ij}(\hat{\mathbf{n}})$ and integrate the resulting equations over the angles to obtain the following system for the components of the order parameter tensor:

$$\begin{aligned} n_{tr} \frac{\partial S_{ij}^{(tr)}}{\partial t} &= -2/3 q_t I u n_{tr} G_{ij;xx}^{(tr)} + \\ &+ \gamma_c n_{cis} (S_{ij}^{(cis)} - S_{ij}^{(tr)}) + \gamma_{tr} n_{tr} (S_{ij}^{(p)} - S_{ij}^{(tr)}), \end{aligned} \quad (28a)$$

$$\frac{\partial S_{ij}^{(p)}}{\partial t} = -\gamma_p n_{tr} (S_{ij}^{(p)} - S_{ij}^{(tr)}), \quad (28b)$$

where $G_{ij;mn}^{(\alpha)}$ is the correlation function of the order parameter components $S_{ij}(\hat{\mathbf{n}})$ and $S_{mn}(\hat{\mathbf{n}})$ that is defined as follows:

$$G_{ij;mn}^{(\alpha)} = \langle S_{ij}(\hat{\mathbf{n}}) S_{mn}(\hat{\mathbf{n}}) \rangle_\alpha - S_{ij}^{(\alpha)} S_{mn}^{(\alpha)}. \quad (29)$$

In addition, we have used the relation

$$P_{tr} - \langle P_{tr} \rangle_{tr} = 2/3 q_t I u (S_{xx}(\hat{\mathbf{n}}) - S_{xx}^{(tr)}), \quad (30)$$

that can be derived from equations (10).

Computing the order parameter correlation functions that enter equations (28) requires the knowledge of the details of the microscopic interactions and, in general, for a non-equilibrium system it can be rather involved and sophisticated. In this paper, we shall adopt the simplest “kinematic” procedure to approximate the correlators that describe the response of the side groups to the pumping light. In our case the part of correlators responsible for out-of-plane reorientation is appeared to be suppressed by polymeric environment, so we shall account for the presence of these constraints by assuming that $G_{ij;xx}^{(tr)} \approx -G_{ij;yy}^{(tr)}$. Then after writing the products of D -functions as a sum of spherical harmonics we neglect the high order harmonics with angular momentum $j > 2$. To this end we can use the known relation for the products of D -functions [38]:

$$D_{m_1 k_1}^{j_1} D_{m_2 k_2}^{j_2} = \sum_j C_{m_1, m_2, m}^{j_1 j_2 j} C_{k_1, k_2, k}^{j_1 j_2 j} D_{m k}^j, \quad (31)$$

where $C_{m_1, m_2, m}^{j_1 j_2 j}$ denotes the Clebsch-Gordon (Wigner) coefficient. In particular, we have

$$\langle S_\alpha^2 \rangle_{tr} \approx 1/5 + 2/7 \langle S_\alpha \rangle_{tr}, \quad \alpha \in \{x, y, z\}. \quad (32)$$

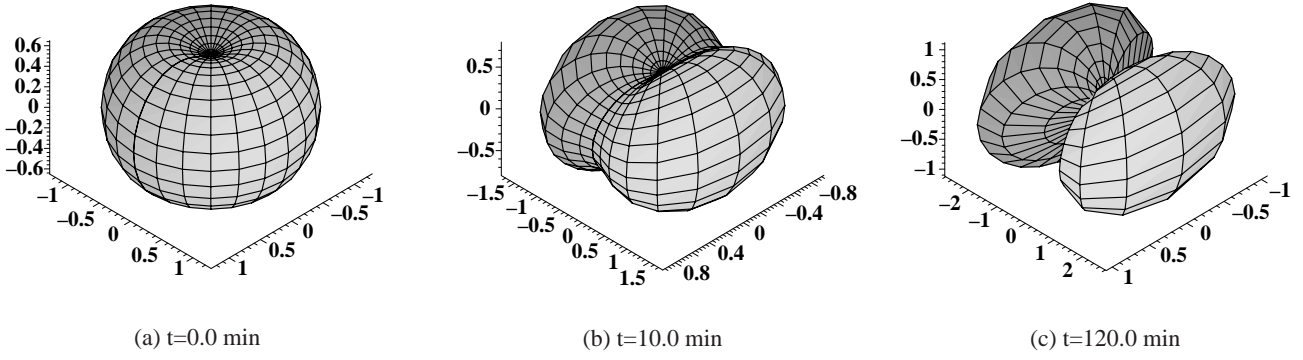


Fig. 7. The orientational distribution functions of *trans* molecules at different illumination doses. These surfaces are defined by the equation $r(\theta, \phi) = 4\pi n_{tr}(t) f_{tr}(\theta, \phi, t)$ in the spherical co-ordinate system at irradiation time t .

Applying this procedure to equations (28) we have the result in the following form:

$$n_{tr} \frac{\partial S}{\partial t} = 2u/3 q_t I (1/5 + 2/7 S - S^2) n_{tr} - \gamma_c n_{cis} S + \gamma_{tr} n_{tr} (S_p - S), \quad (33)$$

$$n_{tr} \frac{\partial \Delta S}{\partial t} = -2u/3 q_t I (2/7 + S) n_{tr} \Delta S - \gamma_c n_{cis} \Delta S + \gamma_{tr} n_{tr} (\Delta S_p - \Delta S), \quad (34)$$

$$\frac{\partial S_p}{\partial t} = -\gamma_p n_{tr} (S_p - S), \quad (35)$$

$$\frac{\partial \Delta S_p}{\partial t} = -\gamma_p n_{tr} (\Delta S_p - \Delta S), \quad (36)$$

where $S \equiv \langle S_y \rangle_{tr}$, $\Delta S \equiv \langle S_x - S_z \rangle_{tr}$, $S_p \equiv \langle S_y \rangle_p$ and $\Delta S_p \equiv \langle S_x - S_z \rangle_p$. Equations (33-36) combined with equation (16) form the system of kinetic equations for our phenomenological model.

3.5 Numerical results

The theoretical curves depicted in Figure 6b are calculated by solving the equations deduced in the previous section: numerical calculations in the presence of irradiation were followed by computing the stationary values of S and ΔS to which the order parameters decay after switching off the irradiation at time t . The initial values of the order parameters $S(0)$ and $\Delta S(0)$ are taken from the experimental data (see the paragraph after Eq. (3)). Since the system is initially at the equilibrium state, the remaining part of the initial conditions is $S_p(0) = S(0)$, $\Delta S_p(0) = \Delta S(0)$, $n_{tr}(0) = 1$ and $n_{cis}(0) = 0$. In addition, we need to take into consideration the difference between the order parameters defined by equation (3) and the order parameters of Section 3.4. Since $D_i \propto (1 + u(2S_i + 1)/3)$, these order parameters differ by the factor $u/(3 + u)$.

From the experimental results of Section 2.4 the lifetime of *cis* molecules τ_c ($\gamma_c = 1/\tau_c$) is about 1.0 s, whereas

the experimental estimate for the other relaxation time characterizing the decay of $D(t)$ to its stationary value after switching off the irradiation is about 4 min. The theoretical value of this relaxation time, deduced from the solution of the kinetic equations without irradiation ($I = 0$ mW/cm²), is $1/(\gamma_p + \gamma_{tr})$. So, in the simplest case, we can assume both the relaxation times τ_p ($\gamma_p = 1/\tau_p$) and τ_{tr} ($\gamma_{tr} = 1/\tau_{tr}$) to be equal to 8 min.

We estimated the absorption cross-sections $\sigma^{(cis)}$ and $\sigma^{(tr)}$ from the UV spectra of the polymer solved in toluene. These spectra were measured before and during irradiation. In the latter case the solution was in the photo-saturated state. The absorption bands were then decomposed into the bands of *trans* and *cis* isomers to yield the corresponding values of the extinction coefficients at $\lambda_t = 365$ nm. In order to compute these coefficients, we followed the procedure described in [39]. The resulting estimates can be written as follows: $(\hbar\omega_t)^{-1} \sigma^{(cis)} \tau_c I \approx 0.2 \times 10^{-2}$ and $\sigma^{(tr)}/\sigma^{(cis)} \approx 2.5$ for $I = 1$ mW/cm², where $\sigma^{(tr)} = (\sigma_{||}^{(tr)} + 2\sigma_{\perp}^{(tr)})/3$ is the average absorption cross-section of the *trans* fragments.

Then, given the experimental value of the order parameter in the photosteady state, $S_{st} = 0.251(1 + 3/u)$, we can relate the anisotropy parameter u and the quantum yield $\Phi_{cis \rightarrow trans}$ through the equation for S_{st} . The latter can be derived from equations (16) and (33) by setting the time derivatives on the left-hand sides equal to zero:

$$\begin{aligned} \gamma_c S_{st} (1 + u(1 - S_{st})/3) &= \\ &= 2u/3 (\gamma_c + q_c I) (1/5 + 2/7 S_{st} - S_{st}^2). \end{aligned} \quad (37)$$

The theoretical curves in Figure 6b are calculated at $\Phi_{cis \rightarrow trans} = 10\%$ and $\Phi_{trans \rightarrow cis} = 5\%$ that is to yield the value of the ratio $\sigma_{||}^{(tr)}/\sigma_{\perp}^{(tr)} = 8.9$. Note that the quantum efficiencies are of the same order of magnitude as the experimental values for other azobenzene compounds [40]. On the other hand, we have $q_c \approx 0.2 \times 10^{-3}$ cm²/mJ that is about the value given in [9].

The computed order parameter components can be used to illustrate the orientational distributions of *trans* fragments maintained after different illumination doses.

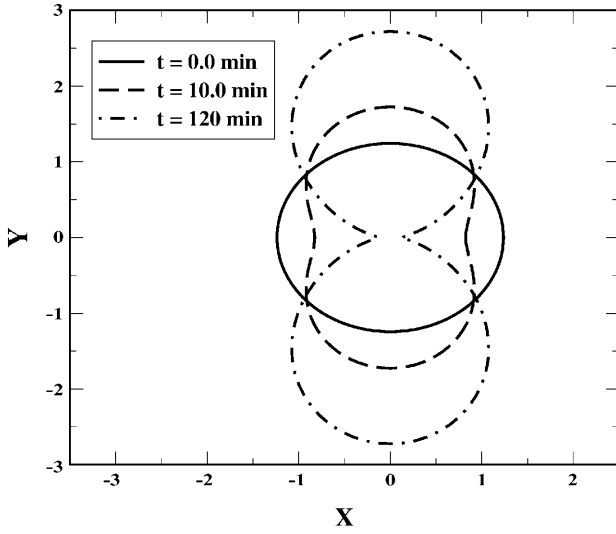


Fig. 8. The initial orientational distribution in section by the x - y plane is isotropic. It assumes anisotropy along the y -axis as the illumination time increases.

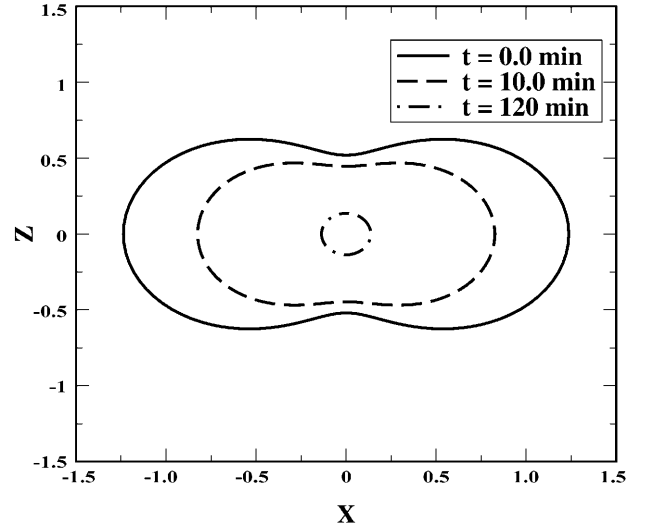


Fig. 9. The increase in the illumination dose renders the orientational distribution of the *trans* fragments in section by the x - z plane isotropic.

Figure 7 shows the surfaces $r(\theta, \phi) = 4\pi n_{tr}(t) f_{tr}(\theta, \phi, t)$ that indicate the angular redistribution in the course of irradiation. Note that we have truncated the expansion for the distribution function f_{tr} by neglecting the high-order spherical harmonics:

$$4\pi f_{tr}(\hat{\mathbf{n}}, t) \approx 1 + 5 \left[\langle S_z \rangle_{tr} D_{00}^2(\hat{\mathbf{n}}) + \frac{\langle S_x \rangle_{tr} - \langle S_y \rangle_{tr}}{\sqrt{6}} 2 \operatorname{Re} D_{20}^2(\hat{\mathbf{n}}) \right]. \quad (38)$$

Sections of the surfaces depicted in Figure 7 by the x - y and x - z co-ordinate planes are shown in Figures 8, 9. As is seen from Figure 8, the angular distribution in the x - y plane becomes anisotropic under the action of light, whereas Figure 9 indicates that the distribution in the x - z plane goes isotropic.

4 Conclusions

In this paper we demonstrate that the combination of the UV/Vis absorption spectroscopy and the suitably modified null ellipsometry method is an appropriate tool for a comprehensive study of POA in films of liquid crystalline polymers with azobenzene side groups.

We found that initially the spin-coated films under investigation are characterized by a preferred in-plane orientation of the azobenzene fragments, whereas the long axes are randomly distributed in this plane. So, the resulting structure is isotropic in this plane, but in the space it is uniaxial with the optical axis normal to the film surface resulting in a negative birefringence (see Sect. 2.4).

Increasing irradiation doses results in an anisotropic order maintained in the film after switching off the linearly polarized UV light. This photoinduced structure corresponds to a biaxial orientational order of the azobenzene

moieties. But it becomes uniaxial at sufficiently large doses reaching the photosaturated state of the photo-orientation process. The process results usually in an oblate order in the case of amorphous polymers. The uniaxiality in the studied case could be related to the liquid crystalline character of the polymer or the initial order of the film which act in combination with the linearly polarized light as aligning force resulting in a uniaxial in-plane order. So, the action of the actinic light can be regarded as a factor stimulating both photo-orientation and thermotropic self-organization.

Quantitatively, experimental results on the kinetics of the photoreorientation were described in terms of the order parameters introduced in Section 2.4. It makes the comparison between experimental and theoretical results relatively direct. On the other hand, it raises the question as to the validity of the procedure used to determine the out-of-plane absorption D_z . In our case this can be justified, for the number of *trans* fragments is shown to remain unchanged in all the relaxed states caused by the lifetime of *cis* isomer. So, the conclusion is that the photoreorientation in the film occurs through the mechanism of angular redistribution. Note that, as a matter of fact, the latter was implicitly assumed in our theoretical model formulated in Section 3.3.

Despite the fact that the theoretical considerations of Section 3 are rather phenomenological, they emphasize the key points that should be addressed by such kind of theories. These are the angular redistribution probabilities (Sect. 3.3) and the order parameter correlation functions (Sect. 3.4). The redistribution operators, in particular, define how the system relaxes after switching off the irradiation and can serve to introduce self-consistent fields. The correlators, roughly speaking, mainly determine the character of photoreorientation and the properties of the photosaturated state.

The assumptions taken in this paper give the model with the kinetics governed by the mechanism of angular redistribution. The form of the approximate correlators influences it in such a way that the out-of-plane reorientation appears to be suppressed.

Our simple model depends on a few parameters that enter the equations and that can be estimated from the experimental data. Only the anisotropy parameter and the quantum yields are derived by making a comparison between the experimental data and the theoretical dependencies.

This theory predicts that the fraction of *cis* isomers is negligible. It is consistent with the assumption that the orientational kinetics of the *cis* fragments governed by equation (27) is irrelevant. The latter is why the liquid crystalline ordering effects [41] that would complicate the kinetics of the *cis* molecules can be safely omitted in equation (27). Note, however, that it is rather straightforward to modify the model for the case where the *cis* fragments would affect the kinetics considerably. We shall extend on this subject elsewhere.

A more detailed microscopic theoretical approach is apparently beyond the scope of this paper. Theoretically, it would be interesting to put this theory into the context of ergodicity-breaking transitions [42]. This work is under progress.

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