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Kinetics of photoinduced anisotropy in azopolymers: models and mechanisms

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Abstract

We consider the effect of photoinduced optical anisotropy (POA) in azopolymers. Using a unified approach to the kinetics of photo-reorientation we discuss the assumptions underlying the known theoretical models of POA and formulate a tractable phenomenological model in terms of angular redistribution probabilities and order parameter correlation functions. The model takes into account biaxiality effects and long-term stability of POA in azopolymers. It predicts that under certain conditions two different mechanisms, photo-orientation and photoselection, will dominate POA depending on the wavelength of pumping light. By using available experimental data, we employ the model to compute dependences of principal absorption coefficients on the illumination time. Our calculations clearly indicate the different regimes of POA and the numerical results are found to be in good agreement with the experimental data.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The ability of some photosensitive materials to become dichroic and birefringent under the action of light is known as the effect of photoinduced optical anisotropy (POA). The effect provides a means of having light-controlled anisotropy and the materials that exhibit POA are very promising for use in many photonic applications [1, 2]. The side-chain polymers that contain covalently linked photochromic moieties such as azobenzene derivatives are among the materials that show POA of extremely high efficiency. For this reason light induced ordering processes in these polymers—the so-called azopolymers—have been intensively studied in the last decade.

A typical experimental procedure to induce optical anisotropy in azopolymers consists in irradiating a sample with polarized UV light. In this case the accepted though not very well understood mechanism of POA assumes that the key processes involved are induced

trans–*cis*-photoisomerization and subsequent thermal and/or photochemical *cis*–*trans*-back-isomerization of the azobenzene moieties.

These *trans*–*cis*–*trans*-photoisomerization cycles are accompanied by rotations of the azobenzene chromophores. Since the transition dipole moment of the azobenzene moiety is directed along its long molecular axis, the fragments oriented perpendicular to the incident actinic light polarization vector, \mathbf{E} , are almost inactive. The long axes of the azobenzene fragments tend to become oriented along directions normal to the polarization vector \mathbf{E} . Non-photoactive groups then undergo reorientation due to co-operative motion or dipole interaction [3–5].

The above scenario, initially suggested in [6], assumes that the *cis*-state becomes temporary populated during photoisomerization but reacts immediately back to thermodynamically stable *trans*-isomeric form. In this regime—the so-called photo-orientation mechanism [7]—the lifetime of *cis*-isomers is short and POA is mainly due to the angular redistribution of the long axes of the *trans*-groups during the *trans*–*cis*–*trans*-isomerization cycles.

Another limiting case occurs when the *cis*-states are long living and POA is caused by the selective depletion of the *trans*-isomeric form when reaching the photosaturated state [8]. This regime of POA is known as the mechanism of angular hole burning (photoselection).

In both cases the effect is primarily governed by the dependence of photoisomerization rates on orientation of the photoactive groups. We have also seen that the physical characteristics of POA can be different depending on a number of additional factors such as the lifetime of the *cis*-form. These factors will determine the kinetics of POA that describes how the amount of photoinduced anisotropy characterized by absorption dichroism or birefringence evolves in time upon illumination and after switching it off.

As opposed to the reversible POA, where anisotropy disappears after switching off the irradiation [2, 6, 7, 9–11], POA can be long-term stable. This is the case for POA in liquid crystalline (LC) azopolymers [12–16]. Theoretically, it means that the photo-reorientation in azopolymers is a non-equilibrium process in a rather complex polymer system and it still remains a challenge to develop a tractable microscopic theory treating the effect adequately.

The microscopic approach to POA in azopolymers can be rather involved and very computationally intensive. In particular, the recent results of [17] show that the nonlinear optical properties of push–pull chromophores embedded in a polymer matrix can be successfully explained on the basis of quantum chemical calculations with taking into account electron–vibration anharmonicity of the chromophores.

In this paper we are primarily interested in phenomenological models that can be employed in studying the kinetics of POA and do not require a sophisticated numerical treatment. Our theoretical considerations rely on the assumption that reorientation of the azobenzene groups results in the appearance of a self-consistent anisotropic field that supports the photoinduced anisotropy. This field is thought of as being caused by anisotropic interactions between the azobenzene fragments and rearrangement of the main chains and other non-absorbing fragments.

There are two phenomenological models based on similar assumptions: the mean-field model proposed in [18, 19] and the model with additional order parameter attributed to the polymer backbone [4, 5]. Both these models, though they look different, incorporate the long-term stability by introducing an additional degree of freedom (subsystem) of which the kinetics reflects the co-operative motion responsible for non-equilibrium behaviour.

In our recent paper [20] we have proposed a model that, in addition to the long-term stability of POA, takes into account biaxiality of the photoinduced orientational structures observed in [13, 16, 20–23]. This model was applied to interpret the experimental data on

POA in the photo-orientation regime for the polymer where the out-of-plane reorientation of the dye molecules is suppressed. The mean-field theory extended to the case of biaxial anisotropy was considered in [23].

The aim of this study is to describe the different regimes of POA on the basis of a unified approach to the kinetics of POA used in [20]. We give more details on the approach and present the theoretical results for the case of long-living *cis*-isomeric form and large order parameters. The layout of the paper is as follows.

In section 2 we discuss the physical assumptions underlying the general structure of phenomenological models. We show that the known models can be rederived in terms of the angular redistribution probabilities and formulate a simple model of the photoinduced ordering in azopolymers. Using the mean-field representation for the angular distribution of *trans*-isomers we suggest the approximation for the order parameter correlation functions and deduce the equations for the order parameter components.

In section 3 we compute the order parameter components and the fractions of the azobenzene units for different irradiation doses. Then we use the results of numerical analysis to fit the experimental data on the photoinduced dichroism of absorption. These data demonstrate that for long-living *cis*-forms dependences of the absorption dichroism on the illumination time can be qualitatively different depending on the wavelength of the exciting beam. We find that the different regimes can be explained by using our model and the calculated dependences are in good agreement with the data obtained experimentally. Finally, in sections 4 and 5 we draw together the results and make some concluding remarks.

2. Model

We shall assume that the azobenzene chromophores in the ground state are of *trans*-form (*trans*-molecules) and the orientation of the molecular axis is defined by the unit vector $\hat{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$, where θ and ϕ are Euler angles of the unit vector. The angular distribution of the *trans*-molecules at time t is characterized by the number distribution function $N_{tr}(\hat{n}, t)$. Similarly, the azobenzene groups in the excited state have the *cis*-conformation (*cis*-molecules) and are characterized by the function $N_{cis}(\hat{n}, t)$. Then the number of *trans*- and *cis*-molecules is given by

$$N_{tr}(t) \equiv N n_{tr}(t) = \int N_{tr}(\hat{n}, t) d\hat{n}, \quad (1)$$

$$N_{cis}(t) \equiv N n_{cis}(t) = \int N_{cis}(\hat{n}, t) d\hat{n}, \quad n_{tr}(t) + n_{cis}(t) = 1, \quad (2)$$

where $\int d\hat{n} \equiv \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta$ and N is the total number of molecules. The normalized angular distribution functions, $f_\alpha(\hat{n}, t)$, of *trans*-($\alpha = tr$) and *cis*-($\alpha = cis$) molecules can be conveniently defined by the relation

$$N_\alpha(\hat{n}, t) = N n_\alpha(t) f_\alpha(\hat{n}, t). \quad (3)$$

We also need to introduce the additional angular distribution function $f_p(\hat{n}, t)$ characterizing the anisotropic field due to interaction between a side chain fragment and nearby molecules. In particular, this field is affected by collective degrees of freedom of non-absorbing units such as main chains and determines the angular distribution of the molecules in the stationary regime. It bears close resemblance to the equilibrium distribution of the mean-field theories of POA. In [18, 19, 23] this distribution has been assumed to be proportional to $\exp(-V(\hat{n})/k_B T)$, where $V(\hat{n})$ is the mean-field potential that depends on the order parameter tensor.

In other words, we have the additional subsystem characterized by $f_p(\hat{n}, t)$ attributed to the presence of long-living angular correlations coming from anisotropic interactions between side-chain groups and collective modes of polymeric environment. For brevity, this subsystem will be referred to as the polymer system (matrix). We shall write the kinetic rate equations for $N_\alpha(\hat{n}, t)$ in the form of master equations [24, 25]:

$$\frac{\partial N_\alpha}{\partial t} = \left[\frac{dN_\alpha}{dt} \right]_{\text{Diff}} + \sum_{\beta \neq \alpha} \int [W(\alpha, \hat{n}|\beta, \hat{n}')N_\beta(\hat{n}', t) - W(\beta, \hat{n}'|\alpha, \hat{n})N_\alpha(\hat{n}, t)]d\hat{n}' + \gamma_\alpha \left[N_\alpha(t) \int \Gamma_{\alpha-p}(\hat{n}, \hat{n}')f_p(\hat{n}', t) d\hat{n}' - N_\alpha(\hat{n}, t) \right], \quad (4)$$

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

The first term on the right-hand side of (4) is due to rotational diffusion of molecules in *trans*- ($\alpha = tr$) and *cis*- ($\alpha = cis$) conformations. In frictionless models this term is absent and will be dropped in our subsequent notations.

Now we need to specify the rate of *trans*–*cis*-photoisomerization stimulated by the incident UV light. For the electromagnetic wave linearly polarized along the x -axis the transition rate can be written as follows [7, 11]:

$$W(cis, \hat{n}|tr, \hat{n}') = \Gamma_{t-c}(\hat{n}, \hat{n}')P_{tr}(\hat{n}'), \quad (5)$$

$$P_{tr}(\hat{n}) = (\hbar\omega_t)^{-1} \Phi_{tr \rightarrow cis} \sum_{i,j} \sigma_{ij}^{(tr)}(\hat{n}) E_i E_j^* = q_t I (1 + un_x^2), \quad (6)$$

where $\sigma^{(tr)}(\hat{n})$ is the tensor of absorption cross section for the *trans*-molecule oriented along \hat{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 $\Gamma_{t-c}(\hat{n}, \hat{n}')$ describes the angular redistribution of the molecules excited in the *cis*-state; I is the pumping intensity and $q_t \equiv (\hbar\omega_t)^{-1} \Phi_{tr \rightarrow cis} \sigma_\perp^{(tr)}$.

A similar line of reasoning applies to the *cis*–*trans*-transition to yield the expression for the rate:

$$W(tr, \hat{n}|cis, \hat{n}') = \gamma_c \Gamma_{c-t}^{(sp)}(\hat{n}, \hat{n}') + q_c I \Gamma_{c-t}^{(ind)}(\hat{n}, \hat{n}'), \quad (7)$$

where $q_c \equiv (\hbar\omega_t)^{-1} \Phi_{cis \rightarrow trans} \sigma^{(cis)}$, $\gamma_c \equiv 1/\tau_c$, τ_c is the lifetime of the *cis*-molecule and the anisotropic part of the absorption cross section is disregarded, $\sigma_\parallel^{(cis)} = \sigma_\perp^{(cis)} \equiv \sigma^{(cis)}$. Equation (7) implies that the process of angular redistribution for spontaneous and stimulated transitions can be different. All the angular redistribution probabilities are normalized so as to meet the standard normalization condition for probability densities:

$$\int \Gamma_{\beta-\alpha}(\hat{n}, \hat{n}') d\hat{n} = 1. \quad (8)$$

Using the system (4) and the relations (5)–(7) it is not difficult to deduce the equation for $n_{tr}(t)$:

$$\frac{\partial n_{tr}}{\partial t} = (\gamma_c + q_c I) n_{cis} - \langle P_{tr} \rangle_{tr} n_{tr}, \quad (9)$$

where the angular brackets $\langle \dots \rangle_\alpha$ stand for averaging over the angles with the distribution function f_α . Owing to the condition (8), this equation does not depend on the form of the angular redistribution probabilities.

The last square bracketed term on the right-hand side of (4) describes the process that equilibrates the side-chain absorbing molecules and the polymer system in the absence of irradiation. The angular redistribution probabilities $\Gamma_{\alpha-p}(\hat{n}, \hat{n}')$ meet the normalization condition, so that thermal relaxation does not change the total fractions N_{tr} and N_{cis} .

If there is no angular redistribution, then $\Gamma_{\alpha-p}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \delta(\hat{\mathbf{n}} - \hat{\mathbf{n}}')$ and both equilibrium angular distributions $f_{tr}^{(eq)}$ and $f_{cis}^{(eq)}$ are equal to f_p .

The latter is the case for the mean-field models considered in [18, 19, 23]. In these models the *cis*-fragments are assumed to be long living with $\gamma_c = 0$ and $\gamma_{cis} = \gamma_{tr}$. We can now recover the models by setting the angular redistribution probabilities $\Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}')$ and $\Gamma_{c-t}(\hat{\mathbf{n}}, \hat{\mathbf{n}}')$ equal to the equilibrium distribution, $f_p = p(\hat{\mathbf{n}})$, determined by the mean-field potential $V(\hat{\mathbf{n}})$: $p(\hat{\mathbf{n}}) \propto \exp(-V/k_B T)$. So, the mean-field approach introduces the angular redistribution operators acting as projectors onto the angular distribution of the polymer system. This is the order-parameter-dependent distribution that characterizes orientation of the azochromophores after isomerization.

An alternative and a more general approach is to determine the distribution function $f_p(\hat{\mathbf{n}}, t)$ from the kinetic equation that can be written in the following form:

$$\frac{\partial f_p(\hat{\mathbf{n}}, t)}{\partial t} = - \sum_{\alpha=\{tr, cis\}} \gamma_p^{(\alpha)} n_\alpha(t) \left[f_p(\hat{\mathbf{n}}, t) - \int \Gamma_{p-\alpha}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_\alpha(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}' \right]. \quad (10)$$

Equations for the angular distribution functions $f_{tr}(\hat{\mathbf{n}}, t)$ and $f_{cis}(\hat{\mathbf{n}}, t)$ can be derived from (4) by using the relations (5)–(9). The result is as follows:

$$\begin{aligned} n_{cis} \frac{\partial f_{cis}}{\partial t} = & -n_{tr} \left[\langle P_{tr} \rangle_{tr} f_{cis} - \int \Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') P_{tr}(\hat{\mathbf{n}}') f_{tr}(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}' \right] \\ & - \gamma_{cis} n_{cis} \left[f_{cis} - \int \Gamma_{cis-p}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_p(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}' \right], \end{aligned} \quad (11)$$

$$\begin{aligned} n_{tr} \frac{\partial f_{tr}}{\partial t} = & -n_{tr} [P_{tr}(\hat{\mathbf{n}}) - \langle P_{tr} \rangle_{tr}] f_{tr} + \gamma_c n_{cis} \int \Gamma_{c-t}^{(sp)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_{cis}(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}' \\ & - (\gamma_c + q_c I) n_{cis} f_{tr} + q_c I n_{cis} \int \Gamma_{c-t}^{(ind)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_{cis}(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}' \\ & - \gamma_{tr} n_{tr} \left[f_{tr} - \int \Gamma_{tr-p}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') f_p(\hat{\mathbf{n}}', t) d\hat{\mathbf{n}}' \right]. \end{aligned} \quad (12)$$

The system of equations (9) and (10)–(12) can be used as a starting point to formulate a number of phenomenological models of POA. We have already shown how the mean-field theories of [18, 19, 23] can be reformulated in terms of the angular redistribution probabilities.

An alternative model was suggested in [4, 5], where the angular distribution of *cis*-isomers is assumed to be stationary and isotropic, $f_{cis} = (4\pi)^{-1}$. The conditions for this assumption to be consistent with equations (10) and (11) are

$$\gamma_{cis} = \gamma_p^{(cis)} = 0 \quad (13)$$

and $\Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = f_{cis}$. To ensure that the equilibrium distribution of *trans*-isomers $f_{tr}^{(eq)}$ is represented by f_p , this model uses the relation

$$\Gamma_{\alpha-p}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \Gamma_{p-\alpha}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \delta(\hat{\mathbf{n}} - \hat{\mathbf{n}}'). \quad (14)$$

The other angular redistribution probabilities defined in [4, 5] are $\Gamma_{c-t}^{(sp)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = f_{tr}(\hat{\mathbf{n}}, t)$ and $\Gamma_{c-t}^{(ind)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = (4\pi)^{-1}$. Neglecting biaxiality is the final step required to obtain the model in the original form.

In this paper we consider another simple model. By contrast to the models [4, 5, 18–20, 23], we take all the angular redistribution operators Γ_{t-c} and Γ_{c-t} in the isotropic form:

$$\Gamma_{c-t}^{(sp)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \Gamma_{c-t}^{(ind)}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \Gamma_{t-c}(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = \frac{1}{4\pi} \equiv f_{iso}. \quad (15)$$

Since the anisotropy of *cis*-fragments has been neglected in (7), it is reasonable to suppose that the equilibrium distribution of *cis*-molecules is also isotropic, $f_{cis}^{(eq)} = f_{iso}$, whereas the equilibrium angular distribution of *trans*-fragments is determined by the polymer system: $f_{tr}^{(eq)} = f_p$. From the above discussion this assumption on the equilibrium state implies using the relations (13)–(14). Equations (9)–(12) can now be combined with (13)–(15) to yield the system of kinetic equations:

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

$$n_{cis} \frac{\partial f_{cis}}{\partial t} = n_{tr} \langle P_{tr} \rangle_{tr} (f_{iso} - f_{cis}), \quad (17)$$

$$\frac{\partial f_p}{\partial t} = \gamma_p n_{tr} (f_{tr} - f_p), \quad (18)$$

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

At this stage we have equation (9) for the fractions and system (16)–(18) for the angular distribution functions. It is now our task to describe the temporal evolution of photoinduced anisotropy in terms of the components of the order parameter tensor [26]

$$S_{ij}(\hat{n}) = 2^{-1} (3n_i n_j - \delta_{ij}). \quad (19)$$

Multiplying (16)–(18) by $S_{ij}(\hat{n})$ and integrating the result over the angles will give a set of equations for the averaged order parameter components $S_{ij}^{(\alpha)} \equiv \langle S_{ij}(\hat{n}) \rangle_\alpha$. The simplest case occurs for the order parameters of *cis*-molecules. From (17) we deduce the equation for $S_{ij}^{(cis)}$:

$$n_{cis} \frac{\partial S_{ij}^{(cis)}}{\partial t} = -n_{tr} \langle P_{tr} \rangle_{tr} S_{ij}^{(cis)}. \quad (20)$$

Rotational diffusion of *cis*-molecules can be taken into account by replacing the coefficient on the right-hand side of (20) with $n_{tr} \langle P_{tr} \rangle_{tr} + 6D_r$, where D_r is the rotational diffusion constant. From (20) and (17) the initially isotropic angular distribution of *cis*-groups, $f_{cis}(0) = f_{iso}$ and $S_{ij}^{(cis)}(0) = 0$, remains unchanged in the presence of irradiation at $t > 0$. In this case the *cis*-molecules will be at equilibrium in the course of irradiation.

By applying the above procedure to (16) and (18) we obtain the following system:

$$n_{tr} \frac{\partial S_{ij}^{(tr)}}{\partial t} = -2/3 q_t I n_{tr} G_{ij;xx}^{(tr)} - n_{cis} (\gamma_c + q_c I) S_{ij}^{(tr)} + \gamma_{tr} n_{tr} (S_{ij}^{(p)} - S_{ij}^{(tr)}), \quad (21)$$

$$\frac{\partial S_{ij}^{(p)}}{\partial t} = -\gamma_p n_{tr} (S_{ij}^{(p)} - S_{ij}^{(tr)}), \quad (22)$$

where $G_{ij;mn}^{(\alpha)}$ is the order parameter correlation function (correlator) defined as follows:

$$G_{ij;mn}^{(\alpha)} = \langle S_{ij}(\hat{n}) S_{mn}(\hat{n}) \rangle_\alpha - S_{ij}^{(\alpha)} S_{mn}^{(\alpha)}. \quad (23)$$

These functions characterize response of the side groups to the pumping light.

Equations (21)–(22) will give the system for the components of the order parameter tensor, if a closure can be found linking the correlation functions and $S_{ij}^{(\alpha)}$. The simplest closure can be obtained by writing the products of the order parameter components as a sum of spherical harmonics and neglecting the high-order harmonics with $j > 2$, where j is the angular momentum number. This is equivalent to truncating the expansion for the angular distribution function f_{tr} over the spherical harmonics. Applying this procedure to the diagonal order

parameter components gives the following parabolic approximation for the order parameter autocorrelators [20]:

$$G_{ii:ii}^{(tr)} \equiv G_{ii} \approx 1/5 + 2/7S_i - S_i^2, \quad S_i \equiv \langle S_{ii} \rangle_{tr}. \quad (24)$$

It is known [26] that the values of S_i lie in the range from -0.5 to 1 and the lowest-order approximation (24) is valid only if S_i is far from the boundary values of the interval $[-0.5; 1]$. Otherwise the approximation fails and the expression on the right-hand side of (24) becomes negative when S_i approaches -0.5 or 1 . Since the autocorrelators G_{ii} must be non-negative, the latter leads to physically absurd results.

The experimental data considered in the subsequent section show that S_x can be about -0.4 . This is well beyond the range of validity of the lowest-order approximation and we need to modify the expression (24). Our assumption is that it can be done by rescaling the order parameter components: $S_i \rightarrow \lambda S_i$, where the coefficient λ can be computed from the condition that there are no fluctuations provided the molecules are perfectly aligned along the co-ordinate unit vector \hat{e}_i : $G_{ii} = 0$ at $S_i = 1$. From (24) the value of λ is $(1 + 0.6\sqrt{30})/7$.

We can estimate the accuracy of this procedure by assuming the Maier–Saupe parametrization for the distribution function f_{tr} :

$$f_{tr} = N^{-1} \exp\left(\sum_{i,j} c_{ij} S_{ij}(\hat{n})\right), \quad (25)$$

$$N = 4\pi \int_0^1 \exp[(c_1 - (c_2 + c_3)/2)(3\tau^2 - 1)/2] I_0(3(c_3 - c_2)(1 - \tau^2)/4) d\tau, \quad (26)$$

where N is the normalization coefficient, c_i are the eigenvalues of the tensor c_{ij} and $I_0(x)$ is the modified Bessel function of the zero order [27]. The representation (25) is taken in the form of distribution functions used in the variational (Maier–Saupe) mean-field theory of liquid crystals [26, 28]. So, the parametrization (25) can be considered as a reasonable approximation for the angular distribution of the mesogenic *trans*-groups in LC azopolymers.

The expression (26) can now be used to compute the order parameters and the correlators as functions of c_i from the formulae

$$S_i = \frac{\partial \ln N}{\partial c_i}, \quad G_{ij} = \frac{\partial^2 \ln N}{\partial c_i \partial c_j}, \quad (27)$$

where $G_{ij} \equiv G_{ii;jj}^{(tr)}$. Equation (27) will yield the dependences $G_{ij}(S_i)$ as functions defined in the parametric form and the accuracy of the modified parabolic approximation can be numerically estimated. Leaving aside the details of numerical calculations, the result is that the mean square relative error is below 5%. So, we have a reasonably good approximation for the correlators of the mean-field distributions (25).

By using the modified parabolic approximation for the correlators, we can write down the resulting system for the diagonal components of the order parameter tensor in the final form:

$$n_{tr} \frac{\partial S}{\partial t} = -2u/3 q_t I (5/7 + 2\lambda/7S - \lambda^2 S^2) n_{tr} - (\gamma_c + q_c I) n_{cis} S + \gamma_{tr} n_{tr} (S_p - S), \quad (28)$$

$$n_{tr} \frac{\partial \Delta S}{\partial t} = 2u/3 q_t I \lambda (2/7 + \lambda S) n_{tr} \Delta S - n_{cis} (\gamma_c + q_c I) \Delta S + \gamma_{tr} n_{tr} (\Delta S_p - \Delta S), \quad (29)$$

$$\frac{\partial S_p}{\partial t} = -\gamma_p n_{tr} (S_p - S), \quad (30)$$

$$\frac{\partial \Delta S_p}{\partial t} = -\gamma_p n_{tr} (\Delta S_p - \Delta S), \quad (31)$$

where $S \equiv \langle S_{xx} \rangle_{tr}$, $\Delta S \equiv \langle S_{yy} - S_{zz} \rangle_{tr}$, $S_p \equiv \langle S_{xx} \rangle_p$ and $\Delta S_p \equiv \langle S_{yy} - S_{zz} \rangle_p$.

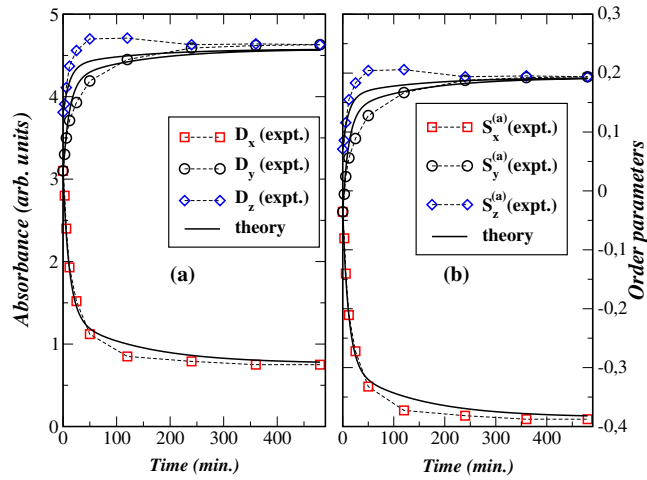


Figure 1. Dependences of (a) the principal absorption coefficients and (b) the absorption order parameters on the irradiation time at $\lambda_{ex} = 488$ nm and $I = 2$ W cm $^{-2}$. Theoretical curves for the order parameters and the absorption coefficients are calculated at $\gamma_c = 0.0$, $r \equiv q_c/q_t = 60.0$, $q_t I = 0.01$ and $u = 38.6$.

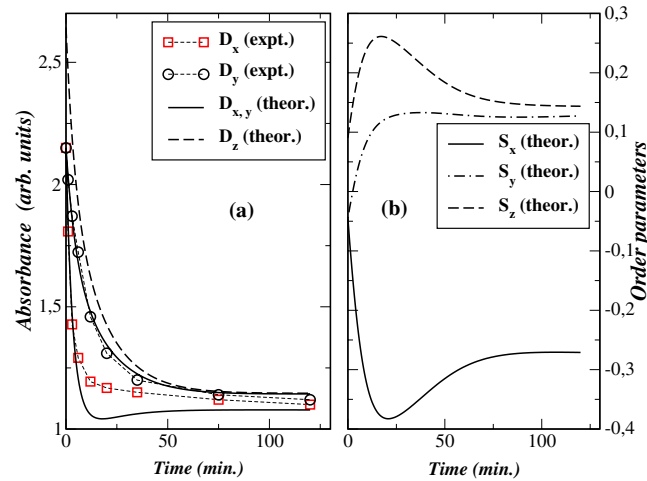


Figure 2. Dependences of (a) the principal absorption coefficients and (b) the order parameter components on the irradiation time at $\lambda_{ex} = 365$ nm and $I = 3$ mW cm $^{-2}$. Theoretical curves for the diagonal components of the order parameter tensor and the absorption coefficients are calculated at $\gamma_c = 0.0$, $r \equiv q_c/q_t = 0.1$, $q_t I = 0.06$ and $u = 8.4$.

3. Numerical results

In this section we demonstrate how our model can be employed to interpret the experimental data of the UV absorption measurements for different irradiation doses. For this purpose we will use the data obtained by Yaroshchuk and co-workers (Institute of Physics of NASU, Ukraine). Since the experimental procedure has been described in [20] and a more comprehensive study is the subject of a joint publication [29], only a brief summary will be given below.

According to [20], the normally incident pumping UV light used in the experiments is propagating along the z -axis and is linearly polarized with the polarization vector \mathbf{E} parallel to

the x -axis. The irradiation was provided in several steps followed by absorption measurements after the waiting time, taken to be longer than 15 min. These measurements were carried out to yield the optical density components D_x and D_y for the testing beam which is linearly polarized along the x - and y -axes, respectively. The wavelength of the testing light was tuned to the absorption maximum of azobenzene chromophores at $\lambda_t = 343$ nm. The principal absorption coefficients D_i can be related to the concentrations and the order parameters as follows:

$$D_i \propto \langle \sigma_{ii}^{(tr)} \rangle_{tr} n_{tr} + \sigma^{(cis)} n_{cis} \propto (1 + u^{(a)}(2S_i + 1)/3)n_{tr} + q_{ct} n_{cis}, \quad (32)$$

where $S_i \equiv \langle S_{ii} \rangle_{tr}$; $u^{(a)}$ is the absorption anisotropy parameter and q_{ct} is the ratio of $\sigma^{(cis)}$ and $\sigma_{\perp}^{(tr)}$ at the wavelength of probing light.

The lifetime of the *cis*-fragments was found to be much longer than the periods examined. So, we can safely take the limit of long-living *cis*-molecules and neglect γ_c in our calculations. In this case the photoselection mechanism discussed in section 1 can be thought to dominate the process of photo-reorientation. There are, however, two sets of experimental data measured at two different wavelengths of the pumping UV light: $\lambda_{ex} = 488$ and 365 nm. These data are shown in figures 1(a) and 2(a), respectively.

Figure 1(a) presents the case in which the wavelength of light is far from the absorption maximum and dependences of the absorption coefficients D_x and D_y on the irradiation time are typical of a photo-orientation mechanism. In this case the fraction of *cis*-molecules is negligible and a sum of all the principal absorption coefficients, $D_{tot} = D_x + D_y + D_z$, does not depend on irradiation doses. For the photosteady state, where $D_y^{(st)} = D_z^{(st)}$, this will yield the relation

$$D_{tot} = D_x^{(st)} + 2D_y^{(st)} = D_x + D_y + D_z. \quad (33)$$

The absorption component D_z depicted in figure 1(a) was estimated by using (33). In addition, figure 1(b) shows the absorption order parameters $S_i^{(a)}$ computed from the expression

$$S_i^{(a)} = \frac{2D_i - D_j - D_k}{2(D_x + D_y + D_z)}, \quad i \neq j \neq k. \quad (34)$$

From (32) with $n_{cis} \approx 0$ these order parameters are proportional to S_i : $S_i^{(a)} = u^{(a)}/(3+u^{(a)})S_i$.

By contrast, referring to figure 2(a), it is seen that both experimental dependences D_x and D_y are decreasing functions of the irradiation time under the wavelength is near the maximum of the absorption band with $\lambda_{ex} = 365$ nm. It indicates that in this case POA is governed by the mechanism of photoselection. So, we have the process of photo-reorientation characterized by two different mechanisms depending on the wavelength of pumping light.

In order to characterize the regime of POA, we can use the fraction of *cis*-fragments in the photo-stationary state. From (9) this fraction is given by

$$n_{cis}^{(st)} = \frac{3 + u(1 + 2S_{st})}{3(r + 1) + u(1 + 2S_{st})}, \quad (35)$$

where $r \equiv (\gamma_c + q_c I)/(q_t I)$, $S_{st} \equiv S_x^{(st)}$ and the corresponding value of the order parameter is a solution of the following equation:

$$2u(1/5 + 2\lambda/7S_{st} - \lambda^2 S_{st}^2) = -S_{st}(3 + u(1 + 2S_{st})), \quad (36)$$

deduced by using equations (28) and (30).

When $\gamma_c = 0$, the parameter r in (35) is the ratio of q_c and q_t . At small values of r it will yield the fraction $n_{cis}^{(st)}$ that is close to unity and we have the kinetics of POA in the regime of photoselection. In the opposite case of sufficiently large values of r the photosteady fraction of *cis*-molecules will be very small, that is typical of the photo-orientation mechanism. This effect is demonstrated in figures 1 and 2. The figures show theoretical curves computed

Table 1. Photochemical parameters.

	$\lambda_{ex} = 365 \text{ nm}$	$\lambda_{ex} = 488 \text{ nm}$
$I \text{ (W cm}^{-2}\text{)}$	3×10^{-3}	2
$\sigma_{cis} \text{ (cm}^2\text{)}$	1.5×10^{-17}	3.14×10^{-18}
$\sigma^{(tr)}/\sigma_{cis}$	57.2	0.5
$\sigma_{\parallel}^{(tr)}/\sigma_{\perp}^{(tr)}$	9.4	39.6
$\Phi_{cis \rightarrow trans} \text{ (\%)}$	15	10
$\Phi_{trans \rightarrow cis} \text{ (\%)}$	10	5

at different values of r : 60.0 and 0.1, respectively. From (35) and (36) the corresponding fractions of *cis*-fragments in the photostationary state can be estimated at about 0.02 and 0.96.

The theoretical curves are computed by solving the rate equations deduced in the previous section. Initial values of the order parameters $S(0)$ and $\Delta S(0)$ are taken from the experimental data measured at $\lambda_{ex} = 488 \text{ nm}$. Since the system is initially at the equilibrium state, the remainder of the initial conditions are $S_p(0) = S(0)$, $\Delta S_p(0) = \Delta S(0)$, $n_{tr}(0) = 1$ and $n_{cis}(0) = 0$.

The anisotropy of the non-irradiated polymer is uniaxial with the optical axis normal to the film surfaces: $S_z^{(a)}(0) = 0.07 > S_x^{(a)}(0) = S_y^{(a)}(0) = -0.035$, whereas the uniaxial structure of the photosaturated state is isotropic in the plane perpendicular to the polarization vector of UV light: $S_x^{(st)} < S_y^{(st)} = S_z^{(st)}$. So, as is shown in figures 1 and 2, the transient anisotropic structures are inevitably biaxial. As in [16, 20–23], these biaxial effects are related to the initial anisotropy of the polymer film and the orientational structure in the photosteady state.

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_0 . The kinetic equations in the absence of irradiation can be easily solved to yield the stationary values of S_i and $S_i^{(p)}$: $(\gamma_p n_{tr}(t_0) S_i(t_0) + \gamma_{tr} S_i^{(p)}(t_0))/\gamma$, where $\gamma \equiv \gamma_p n_{tr}(t_0) + \gamma_{tr}$. There is no further relaxation after reaching this stationary state and its anisotropy is long-term stable. The experimental estimate for the relaxation time characterizing decay of $D_i(t)$ to its stationary value after switching off the irradiation is about 1 h. The theoretical value of this relaxation time is $1/\gamma$. So, in the simplest case, we can assume both relaxation times, τ_p ($\gamma_p = 1/\tau_p$) and τ_{tr} ($\gamma_{tr} = 1/\tau_{tr}$), to be equal to 120 min.

There are a number of additional photochemical parameters that enter the model and are listed in table 1. The table shows the estimates for absorption cross section of *cis*-molecules $\sigma^{(cis)}$ and average absorption cross section of *trans*-fragments, $\sigma^{(tr)} = (\sigma_{\parallel}^{(tr)} + 2\sigma_{\perp}^{(tr)})/3$, obtained from the UV spectra of the polymer dissolved in toluene. We shall omit details on the method of evaluation which is briefly described in [20].

For this polymer the absorption anisotropy parameters and the quantum efficiencies are unknown and need to be fitted. We used the value of S_{st} as an adjustable parameter, so that the anisotropy parameters u and $u^{(a)}$ can be derived from (36) and from the experimental value of the absorption order parameter $S_{st}^{(a)}$ measured at $\lambda_{ex} = 488 \text{ nm}$ in the photosteady state. The numerical results presented in figures 1 and 2 are computed at $u^{(a)} = 11.0$ and $q_{ct} = 2.15$. Note that the quantum efficiencies are of the same order of magnitude as the experimental values for other azobenzene compounds [30].

4. Discussion

The general approach to the kinetics of POA presented in section 2 is based on rather phenomenological considerations. The resulting structure of phenomenological models is

determined by the angular redistribution probabilities. We found that the known models can be formulated by this means. Some of the probabilities define the equilibrium distributions and the relaxation after switching off the irradiation. The angular redistribution operators that enter the photoisomerization rates can be employed to introduce self-consistent fields.

Another key element of our approach is the order parameter correlation functions that enter the equations for the order parameter components. The correlators describe response of the *trans*-molecules to the exciting light and determine the properties of the photosaturated state. We suggested the parabolic approximation to have the correlators expressed in terms of the order parameters. This simple approximation appears to give sufficiently accurate results for the correlators of the angular distribution functions taken in the Maier–Saupe form used in the mean-field theory of liquid crystals. We found that using the parabolic approximation to describe POA in LC azopolymers does not lead to considerable discrepancies between the theory and the experimental data. The approximation, however, cannot be generally valid and a more sophisticated treatment will require the knowledge of the microscopic details to compute the correlators from the Dyson equations.

Our simple model relies on the assumption that the *cis* fragments are isotropic and do not affect the ordering kinetics directly. By contrast to the mean-field models [18, 19, 23], in this case the presence of long-living angular correlations is irrelevant for *cis*-molecules. Certainly, this is the simplest case to start from before studying more complicated models. The model depends on a few parameters that enter the equations and that can be estimated from the experimental data. Only the absorption anisotropy parameters and the quantum yields need to be adjusted.

From the comparison between the experimental data and the theoretical results we can conclude that the theory correctly captures the basic features of POA in azopolymers. The model takes into account the long-term stability of POA and the biaxiality effects. It predicts that in the limit of long-living *cis*-fragments the regime of POA will be governed by the parameter r which is the ratio of $\Phi_{cis \rightarrow trans} \sigma^{(cis)}$ and $\Phi_{trans \rightarrow cis} \sigma_{\perp}^{(tr)}$.

For large values of r the fraction of *cis*-molecules in the photosaturated state is negligible and dependences of the principal absorption coefficients on illumination doses are typical for the kinetics in the regime of photo-orientation. This means that the *cis*→*trans* transitions stimulated by the exciting light will efficiently deplete the *cis*-state and the absorption coefficients are controlled by the terms proportional to the order parameter of *trans*-molecules (see equation (32)).

By contrast, if the value of r is sufficiently small, there is nothing to prevent the *cis*-state from being populated under the action of UV light and the fraction of *cis*-molecules approaches unity upon illumination. In this case the contribution of *trans*-isomers to the absorbance becomes negligible as the illumination dose increases and we have the kinetics of POA dominated by the photoselection mechanism.

We have thus demonstrated that the predictions of the theory are in good agreement with the experimental data, where the difference in the photochemical parameters at $\lambda_{ex} = 365$ and 488 nm can be attributed to the interplay between $\pi\pi^*$ and $n\pi^*$ transitions of the azobenzene moieties. Our findings confirm the conclusion that the dependence of photoisomerization rate on molecular axis orientation (see equations (5) and (6)) plays a leading part in the process of photo-reorientation.

5. Conclusion

The overall strategy used throughout this paper is as follows. We have analysed the general structure of phenomenological models to find out how the models incorporate different physical

assumptions. Then we have studied the simple model and compared the results of calculations with the experimental data.

Recently we have applied this strategy to describe the photo-orientation regime of POA on the basis of the different model that takes into account the presence of additional constraints in the polymer [20]. Since the method turned out to be applicable to the different regimes of POA and to the case of large order parameters, we have a useful tool for studying photoinduced ordering processes in azopolymers.

But even the very possibility to describe the kinetics in terms of one-particle distribution functions needs to be justified by a more detailed theory. The idea of looking for a closure for the correlators is closely related to the mean-field approach. It is likely that this approach can be used to recover the structure of models and we hope that this work will stimulate further progress in this direction.

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