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, photoorientation and photoselection, will dominate POA depending on the wavelength of pumping light. By using available experimental data, we employ the model to compute dependencies 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.

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I. 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). This effect provides a means of having the light-controlled anisotropy and it makes the materials that exhibit POA very promising for use in many photonic applications [1, 2]. Owing to extremely high efficiency of POA in side-chain polymers that contain covalently linked photochromic moieties such as azobenzene derivatives and are known as azopolymers, light induced ordering processes in these polymers have been the subject of intense experimental and theoretical studies in the last decade [3-11].

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 cooperative motion or dipole interaction [3, 10, 11].

The above scenario assumes angular redistribution of the long axes of the trans molecules during the trans–cis–trans isomerization cycles. It is known as the photoorientation mechanism that was initially suggested in Ref. [12] for the case, where the lifetime of cis state is short. This state becomes temporary populated during photoisomerization but reacts immediately back to thermodynamically stable trans isomeric form.

Another limiting case – the so-called angular selective hole burning mechanism (photoselection) – occurs when the cis states are long-living. In this case POA is caused by the selective depletion of the trans isomeric form when reaching

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the steady state \[ \Box \]. The anisotropy induced in this way is not long term stable and disappears as a result of the thermal back reaction.

In both cases the effect is primary governed by the dependence of photosomerization rates on orientation of the photoactive groups. From the other hand, we have also seen that physical characteristics of POA can be different depending on a number of additional factors such as lifetime of the \textit{cis} form. These factors will determine kinetics of POA that describes how amount of photoinduced anisotropy characterized by absorption dichroism or birefringence evolves in time upon illumination and after switching it off.

In particular, as opposed to the reversible POA, where anisotropy disappears after switching off the irradiation \[ \Box \], \[ \Box \], \[ \Box \], \[ \Box \], \[ \Box \], \[ \Box \], \[ \Box \], \[ \Box \] POA can be long term stable. This is the case for POA in liquid crystalline (LC) azopolymers. Theoretically, it means that the photo-reorientation in LC 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.

In this paper we present theoretical considerations concerning the kinetics of POA by starting from kinetic rate equations of general form and assuming that reorientation of the azobenzene groups results in the appearance of a self-consistent anisotropic field that support 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 Ref. \[ \Box \], \[ \Box \] and the model with additional order parameter attributed to the polymer backbone \[ \Box \], \[ \Box \]. Both these models, though they look different, incorporate the long term stability by introducing additional degree of freedom (subsystem) which kinetics reflects cooperative motion and account for non-equilibrium behavior.

In Sec. II we discuss physical assumptions underlying general structure of the phenomenological models and show that it is determined by the angular redistribution probabilities and the order parameter correlation functions. We use the results of general analysis to formulate a simple model of the photoinduced ordering in LC azopolymers. In addition to the long term stability of POA, this model accounts for biaxiality of the photoinduced orientational structures \[ \Box \], \[ \Box \], \[ \Box \], \[ \Box \], \[ \Box \] that was neglected in the models of Refs. \[ \Box \], \[ \Box \], \[ \Box \], \[ \Box \].

In Sec. III we compute order parameter components and fractions of the azobenzene units for different irradiation doses. Then we use the results of numerical analysis to fit the experimental data on photoinduced dichroism of absorption. These data demonstrate that for long-living \textit{cis} forms dependencies of the absorption dichroism on the illumination time can be qualitatively different depending the wavelength of exciting beam. We find that the different regimes can be explained by using our model and the calculated dependencies are in good agreement with the data obtained experimentally.

Finally, in Sec. IV we draw together the results and make some concluding remarks.

II. MODEL

We shall assume that the dye molecules in the ground state are of \textit{trans} form and the orientation of the molecular axis is defined by the unit vector \( \mathbf{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \), where \( \theta \) and \( \phi \) are Euler angles of the unit vector. Angular distribution of the \textit{trans} molecules at time \( t \) is characterized by the number distribution function \( N_{\text{tr}}(\mathbf{n}, t) \). Similarly, molecules in the excited state have the \textit{cis} conformation and are characterized by the function \( N_{\text{cis}}(\mathbf{n}, t) \). Then the number of \textit{trans} and \textit{cis} molecules is given by

\[
N_{\text{tr}}(t) \equiv N_{\text{tr}}(t) = \int N_{\text{tr}}(\mathbf{n}, t) \, d\mathbf{n}, \tag{1}
\]

\[
N_{\text{cis}}(t) \equiv N_{\text{cis}}(t) = \int N_{\text{cis}}(\mathbf{n}, t) \, d\mathbf{n}, \tag{2}
\]

\[
n_{\text{tr}}(t) + n_{\text{cis}}(t) = 1, \tag{3}
\]

where \( \int d\mathbf{n} \equiv \int_{0}^{2\pi} \, d\phi \int_{0}^{\pi} \sin \theta \, d\theta \) and \( N \) is the total number of molecules. The normalized angular distribution functions, \( f_{\alpha}(\mathbf{n}, t) \), of \textit{trans} (\( \alpha = \text{tr} \)) and \textit{cis} (\( \alpha = \text{cis} \)) molecules can be
conveniently defined by the relation

$$N_{\alpha}(\hat{n}, t) = N_{\alpha}(t) f_{\alpha}(\hat{n}, t).$$  (4)

We also need to introduce additional angular distribution function $f_{\alpha}(\hat{n}, t)$ 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 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 Refs. [7] [8] [21] this distribution has been assumed to be proportional to $\exp(-V(\hat{n})/kBT)$, 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 $f_{\alpha}(\hat{n}, t)$ 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, we shall refer to the subsystem as a polymer system (matrix).

We shall write the kinetic rate equations for $N_{\alpha}(\hat{n}, t)$ in the form of master equations [22] [23]:

$$\frac{\partial N_{\alpha}}{\partial t} = \left[ \frac{dN_{\alpha}}{dt} \right]_{\text{Diff}} + \sum_{\beta \neq \alpha} \int \left[ W(\alpha, \hat{n} | \beta, \hat{n}^\prime) \times N_{\beta}(\hat{n}^\prime, t) - W(\beta, \hat{n}^\prime | \alpha, \hat{n}) N_{\alpha}(\hat{n}, t) \right] d\hat{n}^\prime$$

$$+ \gamma_{\alpha} \left[ N_{\alpha}(t) \int \Gamma_{\alpha-p}(\hat{n}, \hat{n}^\prime) f_{p}(\hat{n}^\prime, t) d\hat{n}^\prime \right.$$

$$\left. - N_{\alpha}(\hat{n}, t) \right],$$

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

The first term on the right hand side of Eq. (5) 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 $\rightarrow$ 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 [14] [16]:

$$W(\text{cis}, \hat{n}, tr | \hat{n}, tr^\prime) = \Gamma_{t-c}(\hat{n}, \hat{n}^\prime) P_{tr}(\hat{n}^\prime)$$

$$P_{tr}(\hat{n}) = (\hbar\omega_{t})^{-1} \Phi_{tr-cis} \sum_{i,j} \sigma_{ij}^{(tr)}(\hat{n}) E_{x} E_{x}^{*}$$

$$= q_{t} I (1 + u n_{z}^{2}),$$

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; $\Phi_{tr-cis}$ is the quantum yield of the process and $\Gamma_{t-c}(\hat{n}, \hat{n}^\prime)$ describes the angular redistribution of the molecules excited in the cis state; $I$ is the pumping intensity and $q_{t} \equiv (\hbar\omega_{t})^{-1} \Phi_{tr-cis} \sigma_{\perp}^{(tr)}$.

Similar line of reasoning applies to the cis $\rightarrow$ trans transition, so we have

$$W(\text{tr}, \hat{n}^\prime, cis | \hat{n}^\prime, cis^\prime) = \gamma_{c} \Gamma_{c-t}^{(sp)}(\hat{n}, \hat{n}^\prime)$$

$$+ q_{c} I \Gamma_{c-t}^{(ind)} (\hat{n}, \hat{n}^\prime),$$

where $q_{c} \equiv (\hbar\omega_{c})^{-1} \Phi_{cis-tr} \sigma^{(cis)}$ and $\gamma_{c} \equiv 1/\tau_{c}$, $\tau_{c}$ is the lifetime of cis molecule and the anisotropic part of the absorption cross section is disregarded, $\sigma^{(cis)} = \sigma^{(cis)}_{\parallel} \equiv \sigma^{(cis)}$. Eq. (8) 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

$$\int \Gamma_{\beta-\alpha}(\hat{n}, \hat{n}^\prime) d\hat{n} = 1.$$  (9)

From Eqs. (3), (5) and (8) it is not difficult to obtain equation for $n_{tr}(t)$:

$$\frac{\partial n_{tr}}{\partial t} = (\gamma_{c} + q_{c} I) n_{cis} - \langle P_{tr} \rangle_{tr} n_{tr},$$

where the angular brackets $\langle \ldots \rangle_{\alpha}$ stand for averaging over angles with the distribution function $f_{\alpha}$. Owing to the condition (1), this equation does not depend on the form of the angular redistribution probabilities.

The last square bracketed term on the right hand side of Eq. (9) 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 \(\Gamma_{\alpha-p}(\hat{n}, \hat{n}') = \delta(\hat{n} - \hat{n}')\) and both equilibrium angular distributions \(f^{(eq)}_{tr}\) and \(f^{(eq)}_{cis}\) are equal to \(f_p\).

We can now derive the mean field models considered in Refs. [5, 8, 21] by putting \(\gamma_c = 0\) (long-living cis fragments), \(\gamma_{cis} = \gamma_{tr}\) and assuming that the angular redistribution probabilities \(\Gamma_{t-c}(\hat{n}, \hat{n}')\) and \(\Gamma_{c-t}(\hat{n}, \hat{n}')\) are equal to the equilibrium distribution, \(f_p = p(\hat{n})\), determined by the mean-field potential \(V(\hat{n})\): \(p(\hat{n}) \propto \exp(-V/k_BT)\). In other words, this procedure implies that the angular redistribution operators act as projectors onto the angular distribution of polymer system. This is the order parameter dependent distribution that characterizes the orientation of azo dye molecules after isomerization.

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

\[
\frac{\partial f_p(\hat{n}, t)}{\partial t} = \sum_{\alpha=\{tr,cis\}} \gamma\alpha n_\alpha(t) \left[ f_p(\hat{n}, t) - \int \Gamma_{p-\alpha}(\hat{n}, \hat{n}') f_\alpha(\hat{n}', t) d\hat{n}' \right].
\] (11)

Equations for the angular distribution functions \(f_{tr}(\hat{n}, t)\) and \(f_{cis}(\hat{n}, t)\) can be derived from Eq. (5) by using the relations (6)–(10). The result is as follows

\[
n_{cis} \frac{\partial f_{cis}}{\partial t} = -n_{tr} \left[ \langle P_{tr} \rangle_{tr} f_{cis} - \int \Gamma_{t-c}(\hat{n}, \hat{n}') P_{tr}(\hat{n}', t) f_{tr}(\hat{n}', t) d\hat{n}' \right] - \gamma_{cis} n_{cis} f_{cis} - \gamma_{cis} n_{cis} \left[ f_{cis} - \int \Gamma_{cis-p}(\hat{n}, \hat{n}') f_p(\hat{n}', t) d\hat{n}' \right].
\] (12)

\[
n_{tr} \frac{\partial f_{tr}}{\partial t} = -n_{tr} \left[ \langle P_{tr} \rangle_{tr} f_{tr} + \gamma_c n_{cis} \int \Gamma_{c-t}(\hat{n}, \hat{n}') f_{cis}(\hat{n}', t) d\hat{n}' + q_c I n_{cis} \int \Gamma_{c-t}(\hat{n}, \hat{n}') f_{cis}(\hat{n}', t) d\hat{n}' - \gamma_{tr} n_{tr} \left[ f_{tr} - \int \Gamma_{tr-p}(\hat{n}, \hat{n}') f_p(\hat{n}', t) d\hat{n}' \right] \right].
\] (13)

Eq. (14) and Eqs. (11)–(13) can be regarded as a starting point for the formulation of a number of phenomenological models of POA. We have already shown that these models include the mean field theories considered in Refs. [5, 8, 21].

An alternative model was suggested in Refs. [10, 11], where angular distribution of cis isomers is assumed to be stationary and isotropic, \(f_{cis} = (4\pi)^{-1}\). This assumption implies that

\[
\gamma_{cis} = \gamma_p^{(cis)} = 0
\] (14)

and \(\Gamma_{t-c}(\hat{n}, \hat{n}') = f_{cis}\). In order to ensure that \(f_p = f_{tr}\) at the equilibrium state, this model uses the relation

\[
\Gamma_{\alpha-p}(\hat{n}, \hat{n}') = \Gamma_{p-\alpha}(\hat{n}, \hat{n}') = \delta(\hat{n} - \hat{n}').
\] (15)

So, after neglecting biaxiality we can obtain the results of Refs. [10, 11] by additionally putting \(\Gamma_{sp}(\hat{n}, \hat{n}') = f_{tr}(\hat{n}, t)\) and \(\Gamma_{ind}(\hat{n}, \hat{n}') = (4\pi)^{-1}\).

In this paper we consider another simple model by assuming that all the angular redistribution operators \(\Gamma_{t-c}\) and \(\Gamma_{c-t}\) take the following isotropic form:

\[
\Gamma_{c-t}(\hat{n}, \hat{n}') = \Gamma_{c-t}(\hat{n}, \hat{n}') = \frac{1}{4\pi} \equiv f_{iso}.
\] (16)

Since we have neglected anisotropy of cis fragments in Eq. (8), it is reasonable to suppose that the equilibrium distribution of cis molecules is also isotropic, \(f^{(eq)}_{cis} = f_{iso}\). From the other hand, the equilibrium angular distribution of trans fragments is determined by the polymer
system: \[ f_{tr}^{(eq)} = f_p. \] So, we can use Eqs. (14) – (16) to derive the system of kinetic equations from Eqs. (11) – (13). The result is given by
\[
\begin{align*}
n_{cis} \frac{\partial f_{cis}}{\partial t} &= n_{tr} \langle P_{tr} \rangle_{tr} (f_{iso} - f_{cis}), \quad (17a) \\
n_{tr} \frac{\partial f_{tr}}{\partial t} &= (\langle P_{tr} \rangle_{tr} - P_{tr}) n_{tr} f_{tr} + (\gamma_c + q_c I) \\
&\times n_{cis} (f_{iso} - f_{tr}) + \gamma_{tr} n_{tr} (f_p - f_{tr}), \quad (17b) \\
n \frac{\partial f_p}{\partial t} &= \gamma_p n_{tr} (f_{tr} - f_p), \quad (17c)
\end{align*}
\]
where \( \gamma_p \equiv \gamma_{p(tr)} \).

At this stage we have the equation for the fractions (10) and Eqs. (17) for the angular distribution functions. It is now our task to describe the temporal evolution of photoinduced anisotropy in terms of the averaged components of the order parameter tensor \[24\]
\[
S_{ij}(\hat{n}) = 2^{-1} (3n_i n_j - \delta_{ij}).
\] (18)

The simplest case occurs for the order parameters of cis molecules. Integrating Eq. (17a) multiplied by \( S_{ij}(\hat{n}) \) over angles gives the following result:
\[
\frac{\partial S_{ij}^{(cis)}}{\partial t} = -n_{tr} \langle P_{tr} \rangle_{tr} S_{ij}^{(cis)}, \quad (19)
\]
where \( S_{ij}^{(cis)} \equiv \langle S_{ij}(\hat{n}) \rangle_{\alpha} \). Rotational diffusion of cis molecules can be taken into account by replacing the coefficient on the right hand side of Eq. (19) with \( n_{tr} \langle P_{tr} \rangle_{tr} + 6D_r \), where \( D_r \) is the rotational diffusion constant. In any case, ordering kinetics of cis molecules is irrelevant provided the subsystem of cis groups is initially isotropic. The reason is that photoisomerization does not make angular distribution of cis fragments anisotropic in our model.

We can now multiply Eqs. (17b) and (17c) by \( S_{ij}(\hat{n}) \) and integrate the resulting equations over the angles to obtain the following system:
\[
\begin{align*}
n_{tr} \frac{\partial S_{ij}^{(tr)}}{\partial t} &= -2/3 q_t I u n_{tr} G_{ij;xx}^{(tr)} - n_{cis} \\
&\times (\gamma_c + q_c I) S_{ij}^{(tr)} + \gamma_{tr} n_{tr} (S_{ij}^{(o)} - S_{ij}^{(tr)}), \quad (20a)
\end{align*}
\]
\[
\begin{align*}
n \frac{\partial S_{ij}^{(o)}}{\partial t} &= -\gamma_p n_{tr} (S_{ij}^{(o)} - S_{ij}^{(tr)}), \quad (20b)
\end{align*}
\]
where \( G_{ij;mn}^{(a)} \) is the order parameter correlation function (correlator) defined as follows:
\[
G_{ij;mn}^{(a)} = \langle S_{ij}(\hat{n})S_{mn}(\hat{n}) \rangle_{\alpha} - S_{ij}^{(a)} S_{mn}^{(a)}. \quad (21)
\]
These functions characterize response of the side groups to the pumping light.

Eqs. (20) will give the system for the components of the order parameter tensor, if a closure can be found linking the correlation functions and \( S_{ij}^{(a)} \). 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. In particular, applying this procedure to the diagonal order parameter components gives the following parabolic approximation for the order parameter autocorrelators \[21\]
\[
G_{ii;ii}^{(tr)} \approx 1/5 + 2/7 \langle S_{ii} \rangle_{tr} - \langle S_{ii} \rangle_{tr}^2. \quad (22)
\]

According to the definition (21), the autocorrelators \( G_{ii;ii}^{(tr)} \) must be non-negative. From the other hand, the values of \( \langle S_{ii} \rangle_{tr} \) are ranged from \(-0.5\) to \(1\) \[24\] and the expression on the right hand side of Eq. (22) takes negative values on the specified interval. In order to restore the correct behavior, we need to modify the approximation (22). Our assumption is that it can be done by rescaling the order parameter components: \( \langle S_{ii} \rangle_{tr} \rightarrow \lambda \langle S_{ii} \rangle_{tr} \), where \( \lambda \) is the coefficient that takes into account contributions coming from the high order harmonics. In our calculations we used the largest value of \( \lambda \), \( \lambda_{max} = (1 + 0.6\sqrt{30})/7 \). This implies that there are no fluctuations provided the molecules are perfectly aligned along the coordinate unit vector \( \hat{e}_i \) and \( G_{ii;ii}^{(tr)} = 0 \) at \( \langle S_{ii} \rangle_{tr} = 1 \).

By using the modified parabolic approximation for the correlators, we can now write down the resulting system for the diagonal components of the order parameter tensor in the final form:
\[
\begin{align*}
n_{tr} \frac{\partial S_{ii}}{\partial t} &= -2u/3 q_t I (5/7 + 2\lambda/7 S - \lambda^2 S^2) n_{tr} \\
&\quad - (\gamma_c + q_c I) n_{cis} S + \gamma_{tr} n_{tr} (S_p - S), \quad (23)
\end{align*}
\]
\[
\begin{align*}
n_{tr} \frac{\partial \Delta S}{\partial t} &= 2u/3 q_t I (2/7 + \lambda S) n_{tr} \Delta S - n_{cis} \\
&\quad \times (\gamma_c + q_c I) \Delta S + \gamma_{tr} n_{tr} (\Delta S_p - \Delta S), \quad (24)
\end{align*}
\]
\[
\frac{\partial S_p}{\partial t} = -\gamma_p n_{tr}(S_p - S),
\]
\[
\frac{\partial \Delta S_p}{\partial t} = -\gamma_p n_{tr}(\Delta S_p - \Delta S),
\]
where \( S \equiv \langle S_{xx} \rangle_{tr}, \ \Delta S \equiv \langle S_{yy} - S_{zz} \rangle_{tr}, \ \langle S_{xx} \rangle_p \) and \( \Delta S_p \equiv \langle S_{yy} - S_{zz} \rangle_p \).

### III. 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 Dr. O. Yaroshchuk and co-workers (Institute of Physics of NASU, Ukraine). Since the experimental procedure has been described in Ref. [20] and a more comprehensive study is the subject of joint publication [25], only a brief summary will be given below.

According to Ref. [20], the normally incident pumping UV light used in the experiments is propagating along the x-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 period 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 on the x and y axes, respectively. The wavelength of the testing light was tuned to the absorption maximum of azobenzene chromophores at \( \lambda_t = 343 \text{ nm} \). The principal absorption coefficients \( D_i \) can be related to the concentrations and the order parameters as follows

\[
D_i \propto \langle \sigma_{ii}^{(tr)} \rangle_{tr} n_{tr} + \sigma^{(cis)} n_{cis}
\]
\[
\propto (1 + u^{(a)})(2 S_i + 1)/3 n_{tr} + q_{ct} n_{cis},
\]  
where \( S_i \equiv \langle S_{ii} \rangle_{tr}; \ u^{(a)} \) is the absorption anisotropy parameter and \( q_{ct} \) is the ratio of \( \sigma^{(cis)}_\perp \) and \( \sigma^{(cis)}_\parallel \) at the wavelength of probing light.

The lifetime of the \textit{cis} fragments was found to be much longer than the periods examined. So, we can safely take the limit of long-living \textit{cis} molecules and neglect \( \gamma_c \) in our calculations.

In this case the photoselection mechanism discussed in Sec. I 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: \( \lambda_{ex} = 488 \text{ nm} \) and \( \lambda_{ex} = 356 \text{ nm} \). These data are shown in Fig. [1a] and Fig. [3a], respectively.

Fig. [1a] presents the case in which the wavelength of light is far from the absorption maximum and dependencies of the absorption coefficients \( D_x \) and \( D_y \) on the irradiation time are typical of photoorientation mechanism. In this case the fraction of \textit{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

\[
D_{tot} = D_x^{(st)} + 2D_y^{(st)} = D_x + D_y + D_z.
\]

The absorption component \( D_z \) depicted in Fig. [1a] was estimated by using Eq. (28). In addition, Fig. [1b] shows the absorption order parameters \( S_i^{(a)} \) computed from the expression

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

From Eq. (27) 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 Fig. [2a], it is seen that both experimental dependencies \( D_x \) and \( D_y \) are decreasing functions of the irradiation time under the wavelength is near the maximum of absorption band with \( \lambda_{ex} = 356 \text{ nm} \). 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 \textit{cis} fragments in the photo-stationary state. From Eq. (13) this fraction is given by

\[
n_{cis}^{(st)} = \frac{3 + u(1 + 2S_{st})}{3(r + 1) + u(1 + 2S_{st})},
\]
FIG. 1: Dependencies 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/cm². Theoretical curves for the order parameters and the absorption coefficients are calculated at $\gamma_c = 0.0$, $r \equiv q_c/q_t = 60.0$, $q_I = 0.01$ and $u = 38.6$.

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

$$2u \left( \frac{1}{5} + 2\lambda/7 S_{st} - \lambda^2 S_{st}^2 \right) = -S_{st}(3 + u(1 + 2S_{st})), \quad (31)$$

deducted by using Eqs. (23) and (25).

When $\gamma_c = 0$, the parameter $r$ in Eq. (30) 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 the 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 photoorientation mechanism. This effect is demonstrated in Figs. [1] and [2]. The figures show theoretical curves computed at different values of $r$: 60.0 and 0.1, respectively. From Eqs. (30) and (31) 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 $\lambda_{ex} = 488$ nm. 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 $n_{cis}(0) = 0$.

Numerical calculations in the presence of irradiation were followed by computing the stationary values of $S$ and $\Delta S$ to which the order parameters decay after switching off the irradiation at time $t$. 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, deduced from solution of the kinetic equations in the absence of irradiation, is

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FIG. 2: Dependencies of (a) the principal absorption coefficients and (b) the order parameter components on the irradiation time at $\lambda_{ex} = 365$ nm and $I = 3 \text{ mW/cm}^2$. 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 $u = 8.4$.

$1/(\gamma_p + \gamma_{tr})$. So, in the simplest case, we can assume both relaxation times, $\tau_p (\gamma_p = 1/\tau_p)$ and $\tau_{tr} (\gamma_{tr} = 1/\tau_{tr})$, to be equal 120 min.

| $\lambda_{ex}$ (nm) | 365 | 488 |
|---------------------|-----|-----|
| $I$ (W/cm$^2$)      | 0.003 | 2 |
| $\sigma_{cis} \times 10^{-18}$ (cm$^2$) | 15 | 3.14 |
| $\sigma_{tr} / \sigma_{cis}$ | 57.2 | 0.5 |
| $\sigma_{||} / \sigma_{||}$ | 9.4 | 39.6 |
| $\Phi_{cis\rightarrow trans}$ (%) | 15 | 10 |
| $\Phi_{trans\rightarrow cis}$ (%) | 10 | 5 |

TABLE I: Photochemical parameters.

There are a number of additional photochemical parameters that enter the model and are listed in Table I. The table shows the estimates for absorption cross section of cis molecules $\sigma_{(cis)}$ and average absorption cross section of trans fragments, $\sigma_{(tr)} = (\sigma_{||}^{(tr)} + 2\sigma_{\perp}^{(tr)})/3$, obtained from the UV spectra of the polymer solved in toluene. We shall omit details on the method of evaluation which is briefly described in Ref. [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 Eq. (31) and from the experimental value of the absorption order parameter $S_{st}^{(a)}$ measured at $\lambda_{ex} = 488$ nm in the photosteady state. The numerical results presented in Figs. 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 [26].
IV. DISCUSSION

Despite our theoretical considerations are rather phenomenological they emphasize the key points that should be addressed by such kind of theories. These are the angular redistribution probabilities and the order parameter correlation functions. 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 describe response of trans molecules to the exciting light and determine the properties of the photosaturated state.

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 of Refs. [7, 8, 21], it implies that 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.

After making comparison between the experimental data and the theoretical results we can conclude that the theory correctly captures the basic features of POA in azopolymers. 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 \( \Phi_{\text{cis}\rightarrow\text{trans}}(\sigma_\parallel) \) and \( \Phi_{\text{trans}\rightarrow\text{cis}}(\sigma_\perp) \).

For large values of \( r \) the fraction of cis molecules in the photosaturated state is negligible and dependencies of the principal absorption coefficients on illumination doses are typical for the kinetics in the regime of photoorientation. It means that the cis \( \rightarrow \) 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 Eq. (27)).

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 the 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 accord with the experimental data, where the difference in the photophysical parameters at \( \lambda_{\text{ex}} = 365 \text{ nm} \) and \( \lambda_{\text{ex}} = 488 \text{ nm} \) 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 axes orientation (see Eqs. (5) and (7)) plays a leading part in the process of photo-reorientation.

Our concluding remark concerns an overall strategy used throughout this paper. We have analyzed the general structure of phenomenological models to find out how the models incorporate different physical assumptions. Then we studied the simple model and compared the results of calculations with the experimental data. Recently we have applied this strategy to describe the photoorientation regime of POA in the polymer, where the out-of-plane reorientation of the dye molecules is suppressed [20]. Since the method is found to be applicable to the different regimes of POA, we have a useful tool for studying photoinduced ordering processes in azopolymers. But, not speaking of the parabolic approximation for the correlators, 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 structure of models is likely to be recovered in the mean field approximation [27] and we hope that this work will stimulate further progress in this direction.

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