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# Photo-Orientation of Azobenzene-Containing Liquid-Crystalline Materials by Means of Domain Structure Rearrangement

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A novel mechanism of photo-orientation of azobenzene containing liquid-crystalline materials is proposed. This mechanism is based on the notion of photochemically induced domain rearrangement driven by destabilization of liquid-crystalline phase in light absorbing domains due to photochemical formation of non-mesogenic cis-azobenzene moieties. The experimental evidence of photo-induced movement of a domain boundary is presented, and the velocity of this movement is measured. A mathematical model for photo-orientation of a polydomain azobenzene-containing material is formulated. The values of model parameters for a liquid-crystalline azopolymer have been measured in separate experiments. Theoretical predictions demonstrate quantitative agreement with the experimental observations.

keywords: azobenzene, photo-orientation, photoisomerization, liquid-crystalline polymer

## A. Introduction

The present work is devoted to construction of microscopic mechanism of photo-induced alignment of azobenzene-containing liquid-crystalline substances. This phenomenon is

perspective for development of smart photo-controllable materials and devices for information storage.<sup>1-7</sup> Despite numerous potential and already implemented applications, the detailed understanding of microscopic mechanism of photo-orientation process at the present time is lacking. The existing models of this phenomenon can be divided into several classes.

The first class comprises the models created to describe photo-induced alignment of additives in amorphous solids and liquid solutions. These models are based on the idea that during the elementary act of isomerization a molecule of the chromophore reorients randomly. In this case, anisotropic light absorbance during cycles of light induced trans-to-cis-to-trans isomerization leads to preferential orientation of molecular optical transition dipoles perpendicular to electric vector of irradiating light.<sup>8-13</sup> Anisotropy created by this mechanism is usually not very high. Orientation order parameter in experiments with glassy polymers irradiated with polarized light reaches the value of ca.  $\langle P_2 \rangle \sim -0.1$ .<sup>8-10</sup> Another kinetic peculiarity of this model is the “stretched” ordering kinetics. For example, in the framework of this model the order parameter for non-polarized irradiation theoretically reaches the value  $\langle P_2 \rangle \approx 0.3$  within ~30 characteristic times of photoisomerization, whereas values  $\langle P_2 \rangle \approx 0.5$  and  $\langle P_2 \rangle \approx 0.7$  are achieved within 300 and 20000 of characteristic times of photoisomerization, respectively.

Theoretical models of the second class take into account the existence of at least local molecular orientation order in liquid-crystalline materials. The main idea of these models is emergence of a macroscopic torque on the liquid crystal director as a result of interaction of orientationally non-equilibrium ensemble of excited molecules with mesogenic molecular fragments of the matrix. This idea was suggested by Jánossy<sup>14</sup> to account for anomalously low optical Fréedericksz threshold in dye doped nematics, and by Palto and Durand<sup>15</sup> to describe photo-orientation in azobenzene containing Langmuir-Blodgett films. The proposed driving force of photo-orientation in models of this class is the difference in rotation mobility<sup>16</sup> or in interaction energy<sup>17</sup> for chromophores in ground and excited states. Models based on these assumptions successfully describe director reorientation in low molecular weight liquid-

crystalline materials. However, these models have difficulties in describing photo-alignment in polymer media at relatively low irradiation intensities. For example, the model constructed by Pedersen et al.<sup>18</sup> is shown to reproduce the experimentally observed evolution of optical anisotropy only in case of photo-orientation starting from the metastable disordered state of azobenzene-containing liquid-crystalline material.

Models of the third class assume that photo-orientation is caused by photo-induced rotation diffusion of the chromophores that absorb light most efficiently.<sup>19,20</sup> This idea was first suggested by Albrecht.<sup>21</sup> Application of this model for description of the experimental results meets a number of difficulties. In particular, to account for experimentally observed degrees of photo-induced order one has to assume unrealistically large times of absorbed photon energy dissipation ( $10^{-4}$  s)<sup>19</sup>.

In the preceding work a detailed experimental study of the kinetics of photo-orientation in azobenzene-containing nematic copolymer PAAzo6 has been undertaken.<sup>22</sup> Characteristics of photoisomerization reaction and molecular rotation mobility have been measured. The time dependence of order parameters up to the 6<sup>th</sup> rank in the course of photo-orientation has been determined. The obtained data are suitable for quantitative testing of different photo-orientation models. It has been shown that the existing models of photo-orientation fail to reproduce experimentally observed features of photo-orientation, particularly the rate of photo-induced alignment and the evolution of orientation distribution function. Our experiments also showed that photo-orientation is accompanied by enlarging of liquid crystal domains, which is not described by the existing models.

We suppose that the principal origins of unsuccessful description of experimental features of photo-orientation in the framework of the existing models are the following:

i) treating photo-orientation as a local phenomenon, resulting from the behavior of individual molecules;

ii) considering photo-orientation only inside the homogeneously ordered liquid-crystalline medium.

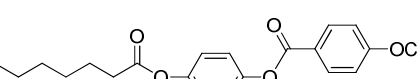
It was observed earlier<sup>6</sup> that photo-orientation is facilitated in case of smaller sizes of LC domains. This observation indicates the important role of processes in the vicinity of domain boundaries. As it has been pointed out,<sup>15</sup> reorientation of the material near domain boundaries can proceed faster due to lower degree of order and lower stability of liquid-crystalline phase in these areas. If domains oriented along the electric vector of light polarization become less stable than the perpendicularly oriented ones, then the process of domain structure rearrangement could lead to photo-orientation.


The present paper is devoted to discussion, elaboration and experimental test of this hypothesis.

## B. Experimental details.

Azobenzene containing liquid-crystalline copolymer PAAzo6 was used as a test subject in the present work. Chemical structure of the copolymer is presented in Fig. 1a. It contains equal amounts of azobenzene and phenylbenzoate groups in the side chains. The synthesis of the polymer is described in detail in Ref. 23. The degree of polymerization for the polymer was about 15, as measured with GPC method. Transition temperatures for this material are 24°C (glass to nematic) and 120°C (nematic to isotropic). For the sample preparation polymer was melted at 120°C, pressed between two glass plates and then cooled to ambient temperature with the rate of ca. 5 °C/min. The film thickness was fixed by PTFE spacers (10 µm thick) placed between the glass plates.

The samples were irradiated with light of high-pressure mercury lamp DRSh-1000 equipped with water IR filter, collimating lens system and a glass filter for isolation of the spectral line 546 nm. This wavelength has been chosen in the range of spectra with low absorbances ( $A \leq 0.5$ ) to ensure homogeneous light intensity throughout the film thickness. Irradiating light intensity

a) 

b) 

UV-vis spectrum of copolymer PAAzo6 in solution is typical for absorbance spectra of trans-azobenzene derivatives. A  $\pi-\pi^*$  band with the maximum at 365 nm and a  $n-\pi^*$  band at 430–600 nm are observed (fig. 1b, black line). Upon irradiation of PAAzo6 in solution, absorption increases in  $n-\pi^*$  band and decreases in  $\pi-\pi^*$  band (fig. 1b, red line). It is well established in literature<sup>24</sup> that these changes are caused by trans-to-cis photochemical isomerization of azobenzene units. This paper deals with the solid films of the polymer with thicknesses 10–30  $\mu\text{m}$ . Only the long-wavelength edge of  $n-\pi^*$  band can be observed in absorbance spectra in this case due to large absorption. Extinction coefficients at 546 nm for azobenzene fragments in the solid material are  $\bar{\epsilon}_t^{546\text{nm}} = 100 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  and  $\bar{\epsilon}_c^{546\text{nm}} = 344 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  for trans- and cis-isomer, respectively<sup>22</sup>.

Photo-orientation in the investigated polymer was found to proceed in the wide temperature range from 5°C to 72 °C ( $T_g=24^\circ\text{C}$ ).

### C. Formulation of photo-orientation mechanism.

The model of photo-orientation proposed in the present work is based on the notion that the orientation of liquid-crystalline material is not spatially uniform. Liquid crystal consists of microscopic areas with various orientations. In the present paper we designate such areas as liquid crystalline domains. Domains with different orientations of the director are separated by transition regions in which director orientation is either undefined (if these areas are disordered) or gradually changes from one direction to another. Strictly speaking, domains and two-dimensional domain walls do not form spontaneously in nematic LC due to high symmetry of these materials.<sup>25,26</sup> However, we will consider the approach, in which relatively large areas with uniform director orientation (domains) are separated by relatively small transition regions (domain boundaries). The concept of domains and domain boundaries is more realistic for description of the structure of LC phases with symmetry lower than nematic (e.g., smectic).

The key assumption of our model is the difference in stability of liquid-crystalline phase in domains with different orientations. This difference serves as a driving force for the process of domain rearrangement. The most probable reason for this difference is the dependence of photostationary concentrations of trans and cis azobenzene units on orientation of the domain director relative to electric field vector of irradiating light.

It is known that the presence of non-mesogenic molecules in liquid-crystalline media leads to destabilization of the liquid crystal phase.<sup>27-29</sup> Trans-azobenzene fragment has anisometric molecular shape, and in some cases, pure azobenzene derivatives form liquid-crystalline phases by themselves.<sup>30,31</sup> At the same time, cis azobenzene unit does not possess rod-like molecular shape. The presence of cis azobenzene derivatives in liquid-crystalline phase leads to its

destabilization. The most vivid manifestation of this effect is the photo-induced phase transition from nematic to isotropic phase as a result of trans-to-cis photoisomerization.<sup>1,32-35</sup>

Figure 2 schematically illustrates the mechanism of photo-orientation proposed here. Two domains are presented, one of them is oriented along the electric field vector of irradiating light, and the other is oriented in a perpendicular direction. The domain of parallel orientation contains trans-azobenzene units ordered in such a way as to effectively absorb irradiating light. As a result, large amount of cis azobenzene units are formed in this domain. On the other hand, trans-azobenzene chromophores in the perpendicularly aligned domain absorb light less effectively and therefore lesser amount of cis-isomer accumulates therein. Higher content of cis isomer results in lower stability of liquid-crystalline phase in the parallel domain, as compared to the perpendicular domain. Reorientation of molecules in the vicinity of domain boundary leads to their transition from one domain to the other so that the relatively less stable domain diminishes and the more stable domain grows. This entails macroscopic preferential alignment of molecules in the direction perpendicular to the electric vector of irradiating light.

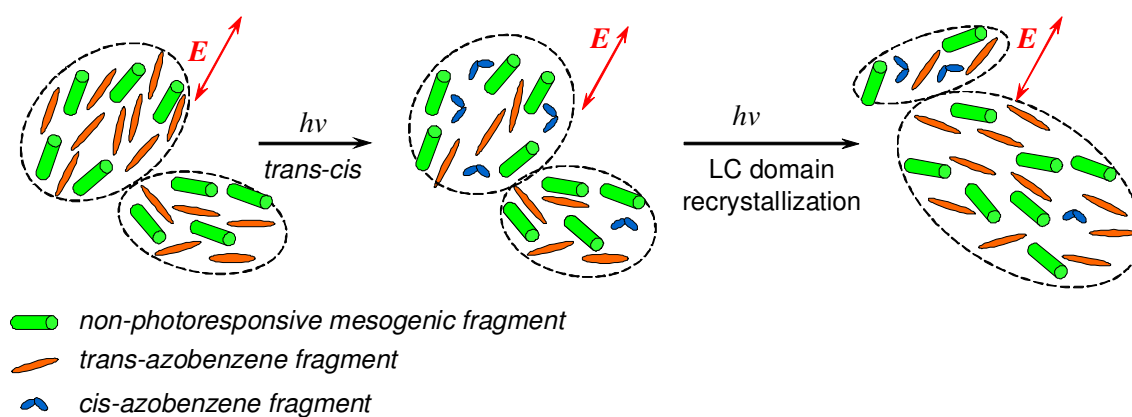


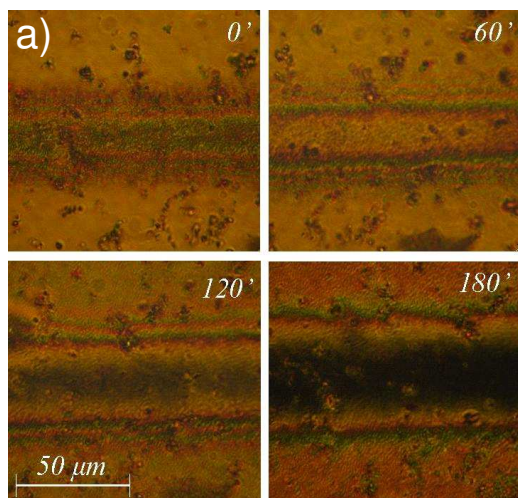
Figure 2. Sketch of the proposed mechanism of photo-orientation (see text).

#### D. Experimental observation of movement of a domain boundary

The following experiment was performed for the verification of the hypothesis about photo-induced motion of domain boundary. A sample of liquid-crystalline copolymer PAAzo6 (see



Section G for experimental details) in form of a film with thickness of 10  $\mu\text{m}$  between two glass plates was aligned by slow cooling in the magnetic field with flux density 1 T. The magnetic field was directed along the film surface. After this the polymer was irradiated with non-polarized light (300 min, 43  $\text{mW}\cdot\text{cm}^{-2}$ ,  $\lambda=546$  nm) through a mask, which was composed of parallel transparent stripes of 15–30  $\mu\text{m}$  width with the distance between stripes of 100  $\mu\text{m}$ . Optical density of dark regions of the mask was no less than 4 O.D. As the result of the irradiation the material under transparent parts of the mask aligned in the direction perpendicular to the sample surface,<sup>22</sup> and the material under the dark stripes of the mask retained original orientation parallel to the film surface. Thus, the sample contained areas with mutually orthogonal director orientations separated by flat surfaces. Figure 3a shows microphotograph of such sample. The region with homeotropic (i. e. along the sample normal) polymer orientation is observed as a dark stripe.



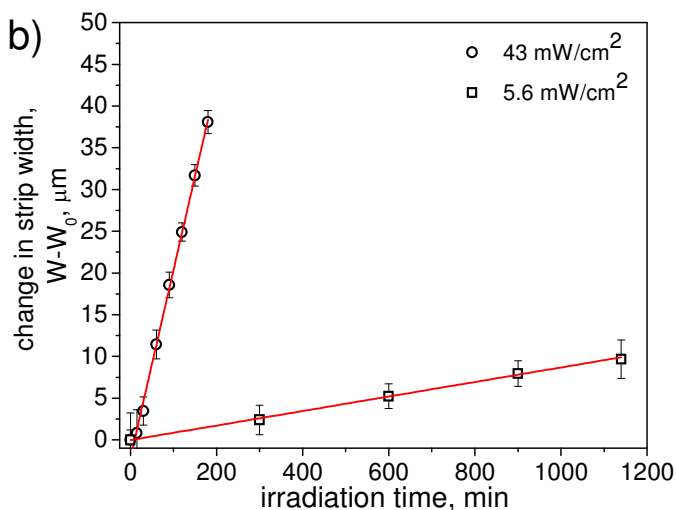


Figure 3. a) Microscopic images between crossed polarizers for the same area of PAAzo6 sample, containing regions with mutually orthogonal LC director orientation; the images were taken at different times of irradiation (light intensity was  $43 \text{ mW}\cdot\text{cm}^{-2}$ ,  $\lambda=546 \text{ nm}$ ) b) dependence of the observed stripe width change in the microscopic image on irradiation time at different light intensities.

Such sample was irradiated then with non-polarized light ( $\lambda=546 \text{ nm}$ ) without a mask. The irradiation was found to induce the increase of the stripe width (fig. 3a). The dependence of stripe width change on irradiation time is plotted in fig. 3b. The velocity of domain boundary movement, defined as half the rate of stripe width change, was found to be  $0.26 \mu\text{m}$  per hour and  $6.8 \mu\text{m}$  per hour for irradiating light intensities  $5.6 \text{ mW}\cdot\text{cm}^{-2}$  and  $43 \text{ mW}\cdot\text{cm}^{-2}$ , correspondingly. Thus, the experiment confirms the occurrence of light induced motion of domain boundary.

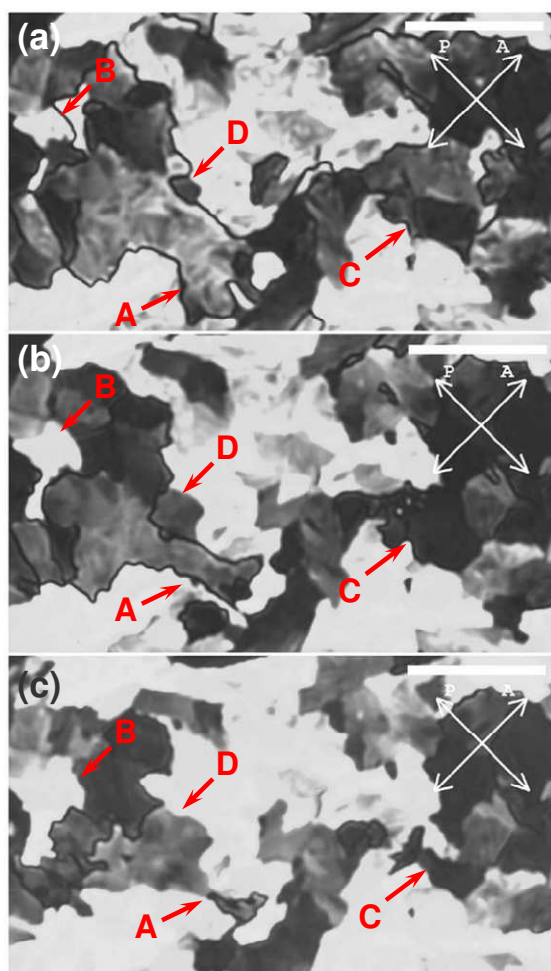


Figure 4. Microphotographs from Ref. 6 showing changes of microscopic textures of the film of azobenzene-containing ionic self-assembly complex during its irradiation with polarized light: initial texture (a), and textures after exposure dose  $0.15 \text{ J}\cdot\text{cm}^{-2}$  (b) and  $3 \text{ J}\cdot\text{cm}^{-2}$  (c). P and A indicate directions of transmission axes of polarizer and analyzer; polarization of irradiating light is horizontal with respect to the picture; scale bar:  $10 \mu\text{m}$ .

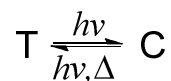
Another experimental confirmation of motion of domain boundaries can be found in the literature. A detailed experimental study of photo-orientation in azobenzene-containing ionic self-assembly complex is reported by Zakrevskyy et al.<sup>6</sup> Inter alia, change in microscopic structure of the material in the course of light irradiation was monitored using polarized optical microscopy. Figure 4 shows the texture change during photo-orientation obtained in Ref. 6. It is seen that the domains marked as A and C diminish in the course of photo-orientation, whereas the domains B and D grow.

### E. Isomerization kinetics and its influence on photo-orientation

The construction of a quantitative model of photo-orientation by the suggested scenario will be started with the discussion of characteristic times of processes involving azobenzene molecular fragment and the detailed consideration of the kinetics of photoisomerization of azobenzene derivatives within anisotropic liquid-crystalline domain.

The absorption of a light photon by a molecule leads to isomerization with the probability equal to the corresponding quantum yield. The complete relaxation of electronic<sup>36</sup> and vibrational<sup>37</sup> excitation proceeds within the time of 10–100 ps. After this the molecule can still be in orientationally non-equilibrium state. Relaxation of molecule orientation in the matrix cage proceeds within the times of  $10^{-11}$ – $10^{-9}$  s.<sup>38,39</sup> This time is needed to establish the equilibrium axial orientation distribution of chromophores according to the mean intermolecular potential of the liquid-crystalline medium. Equilibrium rotational mobility proceeds through cooperative orientational motions which involve the rearrangement of the matrix cage around the chromophores. These rotations have characteristic times  $10^{-9}$ – $10^{-5}$  s in low molecular weight liquid crystals,<sup>39</sup> and can be much slower in liquid-crystalline polymers (up to 100–1000 s).<sup>40,41</sup>

In the absence of absorbance anisotropy, for example for chromophore molecules dissolved in isotropic liquid, the probability of a molecule to absorb light is determined by average molar extinction coefficient  $\bar{\epsilon}$ . The azobenzene chromophore can exist in trans and cis configurations. Trans-to-cis and cis-to-trans isomerization can proceed photochemically, and cis-to-trans isomerization can also proceed thermally, according to the following scheme:



where T and C denote trans- and cis-azobenzene moieties. Consider kinetic equation of isomerization reaction. The rate of isomerization in the approximation of low optical density of the sample is given by the expression:

$$\frac{dx_c}{dt} = I \ln 10 \varphi_{tc} \bar{\varepsilon}_t x_t(t) - I \ln 10 \varphi_{ct} \bar{\varepsilon}_c x_c(t) - k_{ct} x_c(t), \quad (1)$$

where  $x_c$  is the molar fraction of cis isomer,  $x_t$  is the molar fraction of trans isomer,  $I$  is the light intensity expressed in  $\text{Einstein} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ,  $\bar{\varepsilon}_t, \bar{\varepsilon}_c$  are average extinction coefficients of trans and cis azobenzene units,  $\varphi_{tc}, \varphi_{ct}$  are quantum yields of trans-to-cis and cis-to-trans photoisomerization,  $k_{ct}$  is the rate coefficient of thermal cis-to-trans isomerization.

The first two summands in the right-hand side of eq. (1) express the rate of trans-to-cis and cis-to-trans photoisomerization, the third summand expresses the rate of thermal cis-to-trans isomerization. Assuming that the reaction starts from the pure trans isomer, the solution of eq. (1) is given by the following expression:

$$x_c(t) = x_c^{ps} \left[ 1 - \exp(-t / \tau_{ph}) \right], \quad (2)$$

where the photostationary mole fraction of cis-azobenzene fragments is the following:

$$x_c^{ps} = \frac{\varphi_{tc} \bar{\varepsilon}_t}{\varphi_{tc} \bar{\varepsilon}_t + \varphi_{ct} \bar{\varepsilon}_c + k_{ct} / I \ln 10} \quad (3)$$

and the time of establishment of photostationary state is expressed as follows:

$$\tau_{ph} = \left( I \ln 10 (\bar{\varepsilon}_t \varphi_{tc} + \bar{\varepsilon}_c \varphi_{ct}) + k_{ct} \right)^{-1} \quad (4)$$

The value  $(\bar{\varepsilon}_t \varphi_{tc} + \bar{\varepsilon}_c \varphi_{ct})$  in eq. (2)–(4) is ca.  $10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  in case of irradiation of azobenzene derivatives into  $n-\pi^*$  absorption band<sup>24</sup>. Using the irradiation power of  $10 \text{ mW} \cdot \text{cm}^{-2}$  ( $I \approx 4 \cdot 10^{-8} \text{ Einstein} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  at 500 nm) and negligibly slow thermal isomerization, the time of establishment of photostationary state comprises  $\tau_{ph} \approx 10 \text{ s}$ . The characteristic times of photo-orientation process in azobenzene-containing liquid-crystalline polymers is in order of minutes to tens of minutes.<sup>5,19,23,42</sup>

The presented estimations of the characteristic times lead to the following conclusion. The equilibrium orientation distribution of azobenzene fragments in correspondence with the orientation of the surrounding liquid crystal molecules establishes quickly as compared to the

rates of photoisomerization and photo-orientation. This equilibrium orientation distribution will be further denoted as local, to stress that it characterizes molecular orientation within the homogeneously ordered material, and takes no account of possible variations of LC director orientation in different areas of the sample. Since this distribution establishes rapidly, it will be assumed that the chromophores retain the equilibrium local orientation distribution at all times during irradiation. Moreover, at low concentrations of cis azobenzene moieties the degree of orientation order is nearly independent of the mole fractions of isomers, as it is shown in the preceding work<sup>22</sup> with the use of the spin-probe technique.

Anisotropy of light absorption by chromophores in liquid-crystalline material should be considered to determine the concentrations of cis and trans azobenzene units during photoisomerization. The probability of a molecule to absorb light depends on the orientation of the molecule with respect to the light electric field. In the assumption of axially symmetric molecular extinction coefficient tensor of the chromophore, the probability of light absorption for a molecule in a given orientation is determined by the following expression:

$$\varepsilon_{mol} = \varepsilon_{\parallel} \cos^2 \chi + \varepsilon_{\perp} \sin^2 \chi, \quad (5)$$

where  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  are components of molecular extinction coefficient tensor,  $\chi$  is an angle between electric field vector of light and the principal axis of extinction coefficient tensor.

Chromophore molecules inside a homogeneously ordered liquid-crystalline domain are ordered in correspondence with local orientation distribution function  $\rho_L(\beta)$ , defined as the number density of molecules oriented at angle  $\beta$  between the domain director and the axis of molecule extinction coefficient tensor. As shown in Appendix A to Ref. 22, absorbance coefficient averaged over orientation distribution in the case of linearly polarized light is given by

$$\varepsilon(\theta) = \bar{\varepsilon} \cdot [1 + 2d \cdot p \cdot P_2(\cos \theta)] \quad (6)$$

Angle  $\theta$  in the expression (6) is the angle between domain director and electric field vector of light,  $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$  is an average extinction coefficient,  $d = \frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{3\bar{\varepsilon}}$  is molecular dichroism,  $p$  is the local rank two order parameter defined as  $p = A_{0,0}^2 = \int \rho_L(\beta) P_2(\cos \beta) d\beta$ ,  $P_2(\cos \beta) \equiv (3\cos^2 \beta - 1)/2$ .

Different absorbance in domains of various orientations leads to differing photostationary fractions of isomers in these domains. Angular dependent photostationary mole fraction of cis azobenzene units is given by (cf. eq. (3))

$$x_c^{ps}(\theta) = \frac{\varphi_{tc} \varepsilon_t(\theta)}{\varphi_{tc} \varepsilon_t(\theta) + \varphi_{ct} \varepsilon_c(\theta) + \frac{k_{ct}}{I \ln 10}} \quad (7)$$

where  $\varepsilon_t(\theta)$  and  $\varepsilon_c(\theta)$  are absorbance coefficients averaged by orientation distribution for trans and cis azobenzene fragments. Values of  $\varepsilon_t(\theta)$  and  $\varepsilon_c(\theta)$  depend on domain orientation with respect to light electric vector. The following dimensionless parameters can be introduced for clarity:

$$\xi = \frac{\varphi_{tc} \bar{\varepsilon}_t}{\varphi_{tc} \bar{\varepsilon}_t + \varphi_{ct} \bar{\varepsilon}_c + k_{ct} / I \ln 10} \quad (8)$$

$$\kappa = \frac{k_{ct}}{I \ln 10 (\varphi_{tc} \bar{\varepsilon}_t + \varphi_{ct} \bar{\varepsilon}_c) + k_{ct}} \quad (9)$$

The parameters  $\xi$  and  $\kappa$  characterize the rate of trans-to-cis photoisomerization and rate of thermal cis-to-trans isomerization, respectively. The explicit expression for the dependence of photostationary cis-azobenzene fraction on domain orientation can be obtained by combining expressions (6) and (7) with parameters defined by (8)–(9):

$$x_c^{ps}(\theta) = \frac{\xi(1 + 2d_t p_t P_2(\cos \theta))}{\xi(1 + 2d_t p_t P_2(\cos \theta)) + (1 - \xi - \kappa)(1 + 2d_c p_c P_2(\cos \theta)) + \kappa} \quad (10)$$

In eq. (10)  $d_t, d_c$  and  $p_t, p_c$  are values of molecular dichroism and local orientation order parameters for each of the isomers. The values of optical and kinetic characteristics of

photoisomerization process for a test nematic polymer PAAzo6 were measured experimentally in our previous work<sup>22</sup>. These values are listed in Table 1 (columns 1-2). By substituting these values into eq. (10), one can obtain dependence of photostationary concentration of cis azobenzene units on domain orientation (fig. 5, straight line). It can be seen that the content of cis azobenzene fragments differs significantly in domains with different orientations.

Table 1. Characteristics of nematic copolymer PAAzo6 <sup>22</sup>.

Photochemical characteristics		Local order parameters *		Model parameters	
$\varphi_{tc}$	0.16	$A_{0,0}^2$	0.78±0.02	$\xi$	0.066±0.004
$\varphi_{ct}$	0.66	$A_{0,0}^4$	0.506±0.010	$\kappa$	$8 \cdot 10^{-4}$
$\overline{\varepsilon}_t$	$100 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	$A_{0,0}^6$	0.214±0.015	$\tau_{ph}$	0.157 min
$\overline{\varepsilon}_c$	$344 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	$A_{0,0}^8$	0.065±0.006	$B'$	$2.2 \text{ } \mu\text{m} / \text{min}$
$k_{ct}$	$5.1 \cdot 10^{-3} \text{ min}^{-1}$			$R_0$	$2 \text{ } \mu\text{m}$
$d_t p_t$	0.576±0.016			$\beta$	0.1727
$d_c p_c$	0.034±0.017				

\*Local order parameters are taken as the corresponding values for the most ordered sample of PAAzo6 after prolonged (32 hours) photo-orientation.



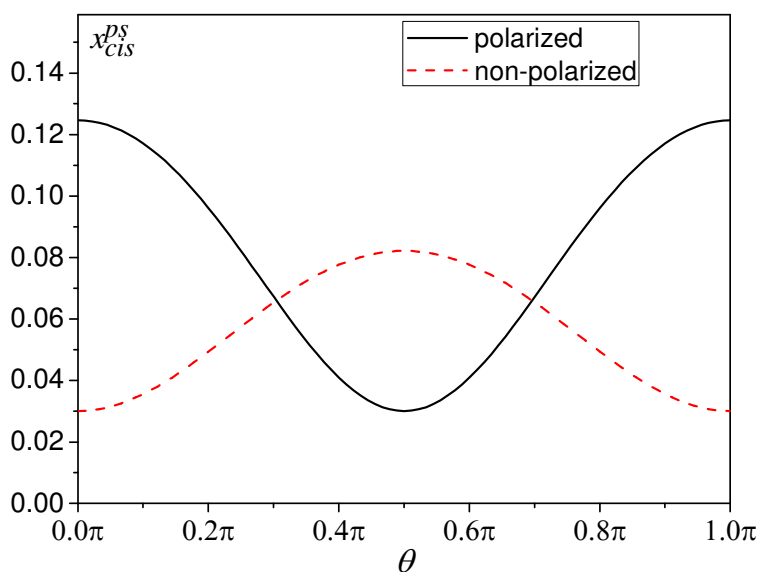


Figure 5. Dependence of photostationary mole fraction of cis azobenzene units on domain orientation upon irradiation with polarized (straight line) and non-polarized (dashed line) light ( $\lambda=546$  nm).

The photo-orientation upon the irradiation with parallel beam of non-polarized light is often considered experimentally.<sup>22,43,44</sup> In these conditions the electric field vector of the light wave is distributed in the plane perpendicular to direction of beam propagation. As it is shown in Appendix A to Ref. 22, the absorbance coefficient averaged by orientation distribution at non-polarized irradiation is equal to

$$\varepsilon(\theta) = \bar{\varepsilon} \cdot [1 - d \cdot p \cdot P_2(\cos \theta)], \quad (11)$$

where  $\theta$  is an angle between light propagation direction and domain director.

Thus, the dependence of photostationary concentration of cis azobenzene units on domain orientation (eq. (7)) can be rewritten in the form:

$$x_c^{ps}(\theta) = \frac{\xi(1 - d_i p_i P_2(\cos \theta))}{\xi(1 - d_i p_i P_2(\cos \theta)) + (1 - \xi - \kappa)(1 - d_c p_c P_2(\cos \theta)) + \kappa} \quad (12)$$

The corresponding dependence calculated using parameters from Table 1 is plotted in fig. 5 (dashed line). It is seen that the dependence of cis-azobenzene concentration on the orientation of

the domain is somewhat weaker under irradiation with unpolarized light than under linearly polarized irradiation.

#### F. Mathematical model of domain structure rearrangement.

A polydomain liquid crystal sample at the initial moment of time can be considered as a set of domains with stochastic orientations. The number of domains with certain orientation in this case is equal to  $N \sin \theta d\theta$ , where  $2N$  is the total number of domains,  $\theta$  is the angle between domain director and electric field vector of light. Each domain is assumed to be homogeneous. The boundary between the domains in the simplest case is assumed to be a 2D surface of zero thickness, to the one side of which the director is oriented at an angle  $\theta_1$ , and to the other side the director is oriented at an angle  $\theta_2$ . Domains of each orientation can be described by mean radius  $R(\theta)$  so that

i) the total volume of domains aligned in the interval of orientations  $\theta \dots \theta + d\theta$  is equal to

$$v(\theta) \sin \theta d\theta = N \cdot (4/3)\pi R^3(\theta) \sin \theta d\theta \quad (13)$$

ii) the total surface area of domains aligned in the interval of orientations  $\theta \dots \theta + d\theta$  is equal to

$$s(\theta) \sin d\theta = N \cdot 4\pi R^2(\theta) \sin \theta d\theta. \quad (14)$$

It is assumed here that the domains are characterized on the average by an effective spherical shape. All domains have the same initial mean radius  $R(\theta)|_{t=0} = R_0$ .

The overall contact area of domains with orientations  $\theta_1 \dots \theta_1 + d\theta_1$  and  $\theta_2 \dots \theta_2 + d\theta_2$  will be denoted as  $\beta(\theta_1, \theta_2) d\theta_1 d\theta_2$ . It is assumed that the relative orientation of adjacent domains is random, therefore the fraction of contact area of domains  $\theta_1$  and  $\theta_2$  in total surface area of domains  $\theta_1$  is equal to the fraction of surface area of domains  $\theta_2$  in total domain surface area.

The following expression is valid in this case:

$$\frac{\beta(\theta_1, \theta_2) \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2}{s(\theta_1) \sin \theta_1 d\theta_1} = \frac{s(\theta_2) \sin \theta_2 d\theta_2}{\int s(\theta) \sin \theta d\theta} \quad (15)$$

This leads to the following expression:

$$\beta(\theta_1, \theta_2) = \frac{s(\theta_1)s(\theta_2)}{\int s(\theta) \sin \theta d\theta} = 4\pi N \frac{R^2(\theta_1)R^2(\theta_2)}{\int R^2(\theta) \sin \theta d\theta} \quad (16)$$

Then the kinetic equation for domain rearrangement process can be derived. Consider the volume of domains with orientations  $\theta \dots \theta + d\theta$ . The rate of volume change due to the domain boundary motion is proportional to free energy difference between adjacent domains and to the contact area:

$$\frac{dv(\theta)}{dt} = B \int (g(x_c(\theta')) - g(x_c(\theta))) \beta(\theta', \theta) \sin \theta' d\theta' \quad (17)$$

The integration in eq. (17) accounts for all possible orientations of adjacent domains,  $g(x_c(\theta))$  is molar Gibbs energy of liquid-crystalline phase in domains with cis isomer fraction  $x_c(\theta)$ ,  $B$  is the transmission coefficient. By substituting expressions (13) and (16) into eq. (17), one can obtain a kinetic equation for the change of mean domain radius for domains with orientation  $\theta$ :

$$\frac{dR(\theta)}{dt} = B \frac{\int (g(x_c(\theta')) - g(x_c(\theta))) R^2(\theta') \sin \theta' d\theta'}{\int R^2(\theta') \sin \theta' d\theta'} \quad (18)$$

According to the hypothesis stated in Section C, the molar free energy of domain is determined by mole fraction of cis-azobenzene units  $x_c(\theta)$  in this domain. The exact form of this dependence is determined by a number of thermodynamic contributions: interaction energies between mesogenic moieties, trans and cis azobenzene fragments, change of entropy due to difference in rotation mobility and rigidity of isomer molecules, difference in effective volumes of isomers<sup>27,28,42,45</sup>. As a first approximation, it is assumed here that the free energy of the liquid-crystalline phase increases linearly with increasing mole fraction of cis-azobenzene moieties,

$g(\theta') - g(\theta) = \alpha(x_c(\theta') - x_c(\theta))$ , where  $\alpha$  is a proportionality coefficient. In this case eq. (18)

can be rewritten as

$$\frac{dR(\theta)}{dt} = B' \frac{\int (x_c(\theta') - x_c(\theta)) R^2(\theta') \sin \theta' d\theta'}{\int R^2(\theta') \sin \theta' d\theta'} , \quad (19)$$

where  $B'$  is the rate of domain volume change through unit contact surface per unit difference in mole fractions of cis isomer in adjacent domains,  $B' = \alpha B$ . The value of  $B'$  for material PAAzo6 can be determined on the basis of the experiment described in Section D. In this experiment the movement of a boundary between the two regions with differing orientations has been observed. Photostationary mole fractions of cis azobenzene units in these two regions can be calculated with eq. (12) using the values of photochemical characteristics listed in Table 1. Photostationary cis content in the domain oriented along the direction of irradiating light propagation is  $x_{c,\parallel} \approx 0.030$ . Photostationary cis content in the domain oriented in the plane of the sample is  $x_{c,\perp} \approx 0.082$ . Then  $B' = 2.2 \mu\text{m}/\text{min}$  and  $B' = 0.083 \mu\text{m}/\text{min}$  in cases of light intensity  $43 \text{ mW}/\text{cm}^2$  и  $5.6 \text{ mW}/\text{cm}^2$ , correspondingly.

The dependence of  $B'$  value on the intensity of irradiating light is presumably caused by the following reason. Consider the process of domain boundary movement. The transition of the material from domain A with large content of cis azobenzene units into domain B with low content of cis azobenzene units leads to higher local concentration of cis isomer near the domain boundary than in the bulk of the domain B. This results in the local decrease of the driving force of photo-orientation. Restoring the concentration difference of cis-azobenzene on the border between the domains takes the time equal to the time of establishment of photostationary state. According to eq. (4), this time is inversely proportional to irradiating light intensity. Thus, the increase of light intensity leads to the more rapid recovery of cis-isomer mole fraction difference near interdomain boundaries and thereby to accelerating of the rearrangement of the domain structure. It is also possible that some heating of the film by high intensity irradiation also causes acceleration of domain boundary movement.

The equation of domain size evolution (19) can be resolved numerically. The following dimensionless variables and parameters are appropriate for simplification of numerical integration:

$$\tau = (I \ln 10 \varphi_{ic} \bar{\varepsilon}_i + I \ln 10 \varphi_{ct} \bar{\varepsilon}_c + k_{ct}) t = t / \tau_{ph} \quad (20)$$

$$r = R / R_0 \quad (21)$$

$$\beta = \frac{\tau_{ph} B'}{R_0} \quad (22)$$

With the use of these notations eq. (19) is rewritten as follows:

$$\frac{1}{\beta} \cdot \frac{dr(\theta)}{d\tau} = \frac{\int (x_c(\theta') - x_c(\theta)) r^2(\theta') \sin \theta' d\theta'}{\int r^2(\theta') \sin \theta' d\theta'} \quad (23)$$

The characteristics measured experimentally in our previous work<sup>22</sup> are suitable for independent determination of values of model parameters. The obtained values are summarized in Table 1 (columns 5–6).

In the experimental conditions<sup>22</sup> the photostationary state of photoisomerization establishes rapidly compared to the photo-orientation process. Photostationary mole fractions of cis azobenzene fragments  $x_c(\theta) = x_c^{ps}(\theta)$  should be used in equation (23) in this case. Since photo-alignment in Ref. 22 is carried out under the action of non-polarized light, photostationary mole fractions of the cis isomer are determined with eq. (12).

Numerical integration of eq. (23) yields the time dependence of the function  $r(\theta)$ , which determines the orientation distribution function of domain directors  $\rho_D(\theta)$  according to the following expression:

$$\rho_D(\theta) \sin \theta = \frac{r^3(\theta) \sin \theta}{\int r^3(\theta') \sin \theta' d\theta'} \quad (24)$$

The time evolution of the function  $\rho_D(\theta)$  (fig. 6a) can be used to obtain theoretical predictions for all characteristics of photo-orientation: experimentally observed order parameters, domain sizes, values of absorbance. The experimentally observed orientation distribution function of the

material is the convolution of local orientation distribution inside a domain  $\rho_L(\theta)$  and the orientation distribution of domain directors  $\rho_D(\theta)$ . The values of orientation order parameters of the whole sample are then calculated as follows:

$$\langle P_J \rangle = A_{0,0}^J \cdot \int P_J(\cos \theta) \rho_D(\theta) \sin \theta d\theta, \quad (25)$$

where  $P_J(\cos \theta)$  are Legendre polynomials of rank  $J$ .  $A_{0,0}^J$  are local order parameters for molecules inside the domain. Values  $A_{0,0}^J$  measured in <sup>22</sup> with the spin probe technique are listed in Table 1 (columns 3–4). Fig. 6b (right-hand scale) shows the calculated time dependence of the sample order parameters. The evolution of mean domain radius, calculated with the expression

$$\langle r \rangle = \int r(\theta) \rho_D(\theta) \sin \theta d\theta \quad (26)$$

is presented in fig. 6c. The overall photostationary concentration of cis-azobenzene within the sample is calculated using the following expression:

$$x_c^\Sigma = \int x_c^{ps}(\theta) \rho_D(\theta) \sin \theta d\theta \quad (27)$$

The light absorbance is described by the expression:

$$D(t) = \int \left( (1 - x_c(\theta, t)) \varepsilon_t(\theta) + x_c(\theta, t) \varepsilon_c(\theta) \right) l c_0 \cdot \rho_D(\theta, t) \sin \theta d\theta \quad (28)$$

Fig. 6b (left-hand scale, lines) shows the kinetic curve of overall mole fraction of cis azobenzene within the sample. This kinetic curve consists of two branches. The first branch represents the initial increase in the mole fraction of cis-azobenzene fragments during the establishment of photostationary state. The kinetic curve in this region is calculated with use of eq. (2). This curve describes the kinetics of cis fraction in the range of dimensionless times  $\tau \lesssim 5$ . The second branch ( $\tau \gtrsim 5$ ) was calculated with eq. (27). This curve shows that the total concentration of cis-azobenzene fragments slowly decreases due to photo-orientation and corresponding accumulation of domains with low photostationary cis content. It can be seen that photo-orientation is accompanied with a significant (twofold) decrease in the total mole fraction

of cis-azobenzene fragments in the sample. This is consistent with our assumption that the change of the mole fraction of cis-azobenzene is the driving force of photo-orientation.

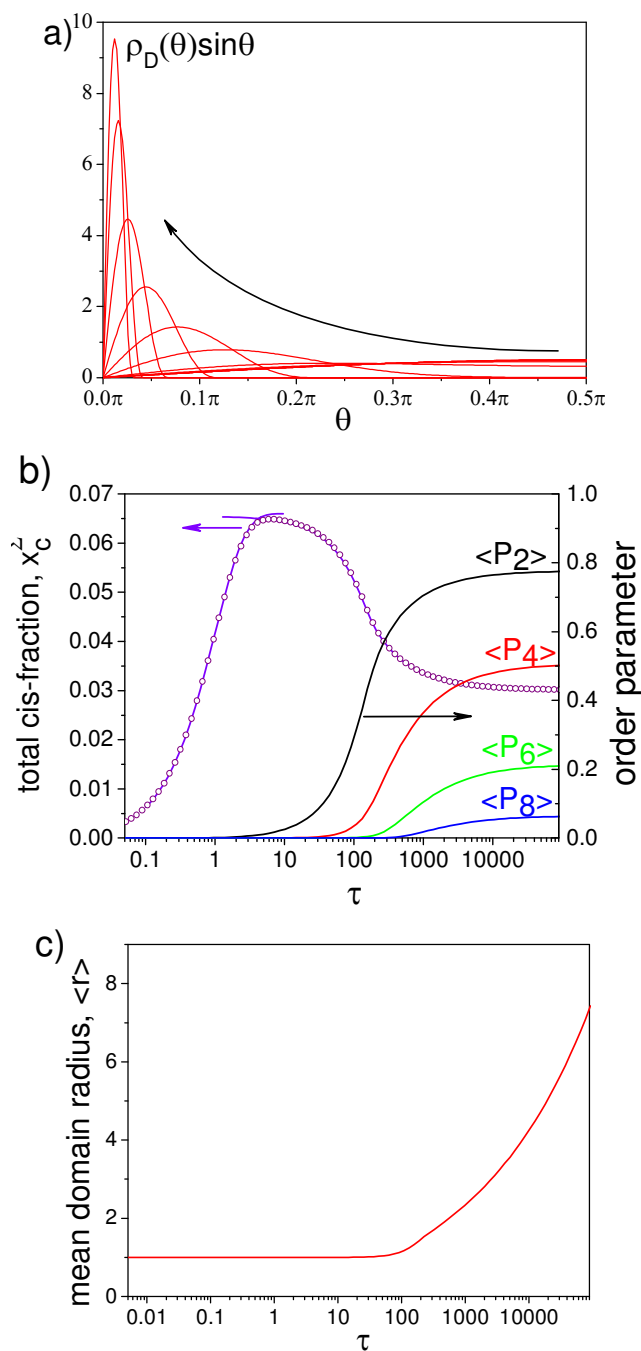


Figure 6. Modeling of photo-orientation upon the action of non-polarized light by eq. (23) with experimentally measured parameters (Table 1). a) Evolution of distribution function of domain orientations; b) kinetics of change of orientation order parameters (right-hand scale) and total cis isomer fraction (left-hand scale); c) kinetics of mean domain radius change.

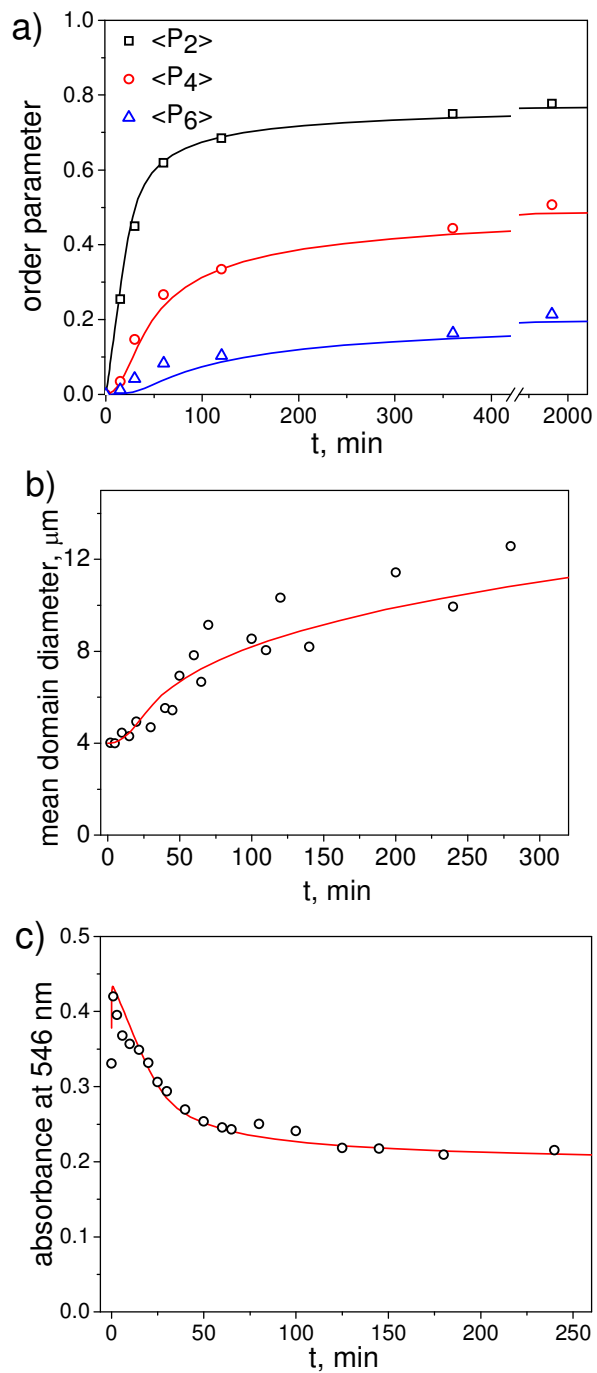


Figure 7. Comparison of predictions of model (23) with experimental measurements<sup>22</sup> for photo-orientation of PAAzo6; a) kinetics of orientation order parameters, b) kinetics of mean domain size change, c) kinetics of absorbance change at irradiation wavelength ( $\lambda=546$  nm).

The numerical results presented in fig. 6a,b indicate that the developed model indeed predicts photo-orientation, i. e. the preferential alignment of domains along the irradiating light



propagation direction. The solution of eq. (23) is compared in fig. 7 with experimental results.<sup>22</sup> Fig. 7a illustrates the kinetics of order parameter change in the course of photo-orientation. The experimental values were obtained with the use of the spin probe technique. The experimental kinetics of mean domain size is compared to the model predictions in fig. 7b. Fig. 7c illustrates the agreement of the predicted optical density (eq. (28)) in the course of photo-orientation with the experimentally measured.

It is seen that the model predictions are confirmed quantitatively by a large set of experimental data obtained by optical absorption spectroscopy, spin probe technique and polarizing optical microscopy. All parameters used in the modeling were determined or estimated from independent experiments, no fitting parameters were used. It should be noted that the proposed formulation of the model contains some geometric simplifications, in particular, the assumption of an effective spherical shape of domains. In addition, the used values of domain sizes should be treated as estimates due to the rough definition of the concept of domain and inter-domain boundary in a nematic material. Despite this, modeling results presented in fig. 7 illustrate the possibility of a quantitative description of experimental data.

So far it has been assumed that the photostationary state of trans-to-cis isomerization establishes quickly compared to the rate of domain rearrangement. This assumption has been used in simulations according to the eq. (23) as the mole fractions of cis isomer were substituted by their photostationary values. In some cases, though, it might be useful to explicitly take into account the kinetics of photoisomerization. As shown in the Appendix, the rate of cis fraction change is determined by the expression:

$$\begin{aligned} \frac{dx_c(\theta)}{d\tau} = & \xi(1-x_c(\theta))\frac{\varepsilon_t(\theta)}{\bar{\varepsilon}_t} - (1-\xi-\kappa)x_c(\theta)\frac{\varepsilon_c(\theta)}{\bar{\varepsilon}_c} - \kappa x_c(\theta) + \\ & + \frac{3\beta}{r(\theta)} \cdot \frac{\int_{x_c(\theta') > x_c(\theta)} [x_c(\theta') - x_c(\theta)]^2 r^2(\theta') \sin \theta' d\theta'}{\int r^2(\theta') \sin \theta' d\theta'} \end{aligned} \quad (29)$$

The first two terms in equation (29) express the rate of change in the cis fraction due to photochemical transformations and the third term is the rate of thermal isomerization. The last term in expression (29) is the rate of cis fraction change in domains oriented at an angle  $\theta$  as a result of the accession of material from domains oriented at an angle  $\theta'$ . Eqs. (23) and (29) form a closed system of differential equations. The solution of these equations with the parameters given in Table 1 reproduces the evolution of order parameters and the size of domains obtained at the using photostationary values of  $x_c(\theta)$ . In fig. 6b (left-hand scale) circles represent the cis fraction changes obtained by explicitly solving eqs. (23) and (29). It is seen that approximate and exact kinetic curves almost coincide. This indicates that the assumption of rapid establishment of photostationary state is justified in this case.

The process of re-orientation of initially ordered material can also be rationalized in the framework of our model. Re-orientation originates on defects, which are always present in the real material. The growth of domains with favorable orientations starts on these defects. However, quantitative description of this process is problematic due to uncertainty in the initial concentration of defects, which is hard to measure experimentally.

## G. Conclusions.

The photo-orientation mechanism based on the assumption of light induced rearrangement of the domain structure of azobenzene-containing liquid-crystalline materials is proposed in the present work. The hypothesis about the photo-induced movement of domain boundary is confirmed experimentally. A kinetic model of photo-orientation is constructed on the basis of the proposed mechanism.

It is known that photo-orientation characteristics are determined by numerous structural properties of the material. The influence of structural factors is implicitly included in our model through kinetic and dynamic parameters listed in Table 1, in the following way:

1  
2 1) chemical structure and reactivity of the isomers, their aggregation and the polymer free  
3 volume are taken into account through the values of quantum yields, extinction coefficients and  
4 optical anisotropies of the isomers, which were measured in separate experiments;  
5  
6

7  
8 2) molecular shapes, intermolecular interaction and its change upon isomerization determine  
9 the thermodynamic driving force for the photo-orientation process; these factors influence the  
10 kinetics of photo-orientation through the experimentally determined value of  $B'$ ;  
11  
12

13 3) rotation mobility of mesogenic units, and the rate of the establishment of photostationary  
14 state also influence the rate of photo-isomerization through the value of  $B'$ ;  
15  
16

17 4) thermal history, annealing and aging of the polymer on photo-orientation lead to the  
18 modification of LC domain sizes<sup>6</sup>, and thus is incorporated in our model.  
19  
20

21 All parameters explicitly included in our model were measured or estimated from independent  
22 experiments for azobenzene-containing nematic polymer. The photo-orientation characteristics  
23 calculated with use of the proposed model and the experimental findings are in good quantitative  
24 agreement.  
25  
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39 calculations were performed with the use of Lomonosov Supercomputer at Moscow State  
40 University.  
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### 48 49 **Supporting information** 50

51 Detailed derivation of eq. (29) is given in the Appendix. This material is available free of  
52 charge via the Internet at <http://pubs.acs.org> .  
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TOC-Graphic

