

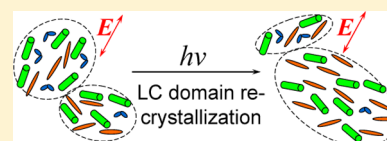
Photo-Orientation of Azobenzene-Containing Liquid-Crystalline Materials by Means of Domain Structure Rearrangement

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S Supporting Information

ABSTRACT: 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 photoinduced 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.



A. INTRODUCTION

The present work is devoted to construction of the microscopic mechanism of photoinduced alignment of azobenzene-containing liquid-crystalline substances. This phenomenon is perspective for development of smart photocontrollable materials and devices for information storage.^{1–7} Despite numerous potential and already implemented applications, the detailed understanding of the microscopic mechanism of the 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 photoinduced 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 the electric vector of irradiating light.^{8–15} Anisotropy created by this mechanism is usually not very high. The orientation order parameter in experiments with glassy polymers irradiated with polarized light reaches the value of ca. $\langle P_2 \rangle \sim -0.1$.^{8–10} 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 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 an orientationally non-equilibrium ensemble of excited molecules with mesogenic molecular fragments of the matrix. This idea was suggested by

Jánossy¹⁴ to account for the anomalously low optical Fréedericksz threshold in dye doped nematics and by Palto and Durand¹⁵ 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 mobility¹⁶ or in interaction energy¹⁷ 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 photoalignment in polymer media at relatively low irradiation intensities. For example, the model constructed by Pedersen et al.¹⁸ is shown to reproduce the experimentally observed evolution of optical anisotropy only in the 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 photoinduced rotation diffusion of the chromophores that absorb light most efficiently.^{19,20} This idea was first suggested by Albrecht.²¹ Application of this model for description of the experimental results meets a number of difficulties. In particular, to account for experimentally observed degrees of photoinduced order, one has to assume unrealistically large times of absorbed photon energy dissipation (10^{-4} s).¹⁹

In the preceding work, a detailed experimental study of the kinetics of photo-orientation in azobenzene-containing nematic copolymer PAAzo6 has been undertaken.²² Characteristics of photoisomerization reaction and molecular rotation mobility have been measured. The time dependence of order parameters up to the sixth rank in the course of photo-orientation has been determined. The obtained data are suitable for quantitative

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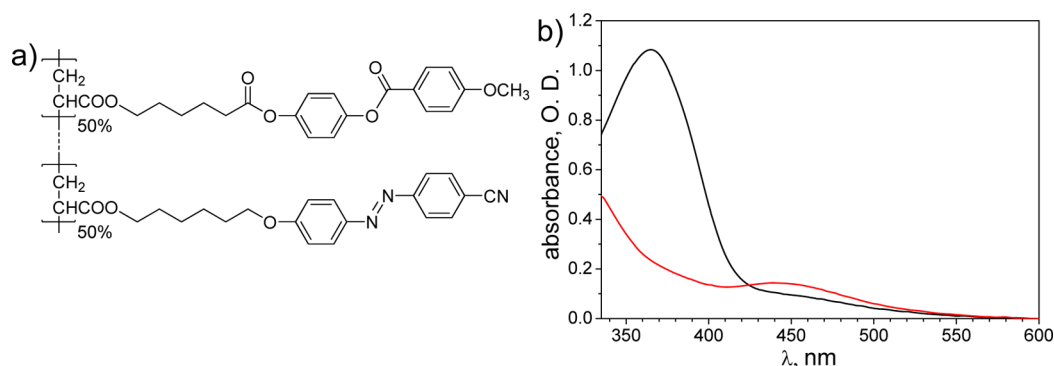


Figure 1. (a) Chemical structure of copolymer PAAzo6, used in the present work. (b) Absorbance spectra of copolymer PAAzo6 dissolved in chloroform. Black line, trans isomer (solution before irradiation); red line, photostationary state with high content of cis isomer (solution irradiated with 365 nm light).

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 photoinduced 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 earlier⁶ that photo-orientation is facilitated in the 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,¹⁵ reorientation of the material near domain boundaries can proceed faster due to the lower degree of order and lower stability of the 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. The chemical structure of the copolymer is presented in Figure 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 the 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 a 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 a water IR filter, a 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 was changed with the use of neutral density filters. The non-attenuated light intensity, measured with a photodiode Vishay-BPW21R, was 43 $\text{mW}\cdot\text{cm}^{-2}$ (1.2×10^{17} photons $\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$). Microscopic images were obtained with polarizing optical microscopes MIN-8 and Axioscope 40Pol (Carl Zeiss) equipped with CCD cameras.

The 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 an $n-\pi^*$ band at 430–600 nm are observed (Figure 1b, black line). Upon irradiation of PAAzo6 in solution, absorption increases in the $n-\pi^*$ band and decreases in the $\pi-\pi^*$ band (Figure 1b, red line). It is well established in the literature²⁴ 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 of 10–30 μm. Only the long-wavelength edge of the $n-\pi^*$ 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.²²

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

C. FORMULATION OF THE 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.^{25,26} 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

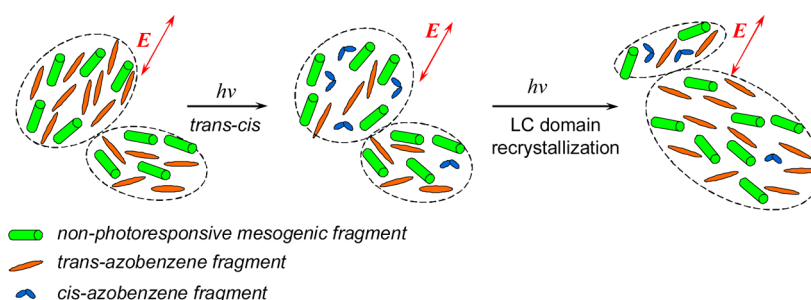


Figure 2. Sketch of the proposed mechanism of photo-orientation (see text).

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 the 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 the orientation of the domain director relative to the 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.^{27–29} The *trans*-azobenzene fragment has anisometric molecular shape, and in some cases, pure azobenzene derivatives form liquid-crystalline phases by themselves.^{30,31} At the same time, the *cis*-azobenzene unit does not possess a rod-like molecular shape. The presence of *cis*-azobenzene derivatives in the liquid-crystalline phase leads to its destabilization. The most vivid manifestation of this effect is the photoinduced phase transition from nematic to isotropic phase as a result of *trans*-to-*cis* photoisomerization.^{1,32–35}

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, a 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 a lesser amount of *cis* isomer accumulates therein. A higher content of *cis* isomer results in a lower stability of the liquid-crystalline phase in the parallel domain, as compared to the perpendicular domain. Reorientation of molecules in the vicinity of the 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.

D. EXPERIMENTAL OBSERVATION OF MOVEMENT OF A DOMAIN BOUNDARY

The following experiment was performed for the verification of the hypothesis about photoinduced motion of the domain boundary. A sample of liquid-crystalline copolymer PAAzo6 (see section B for experimental details) in the form of a film with a thickness of 10 μm between two glass plates was aligned by slow cooling in the magnetic field with a flux density of 1 T. The magnetic field was directed along the film surface. After

this, the polymer was irradiated with non-polarized light (300 min, 43 $\text{mW}\cdot\text{cm}^{-2}$, $\lambda = 546 \text{ nm}$) through a mask, which was composed of parallel transparent stripes of 15–30 μm width with the distance between stripes of 100 μm . The optical density of dark regions of the mask was no less than 4 O.D. As a result of the irradiation, the material under transparent parts of the mask aligned in the direction perpendicular to the sample surface,²² and the material under the dark stripes of the mask retained the original orientation parallel to the film surface. Thus, the sample contained areas with mutually orthogonal director orientations separated by flat surfaces. Figure 3a shows a microphotograph of such sample. The region with homeotropic (i.e., along the sample normal) polymer orientation is observed as a dark stripe.

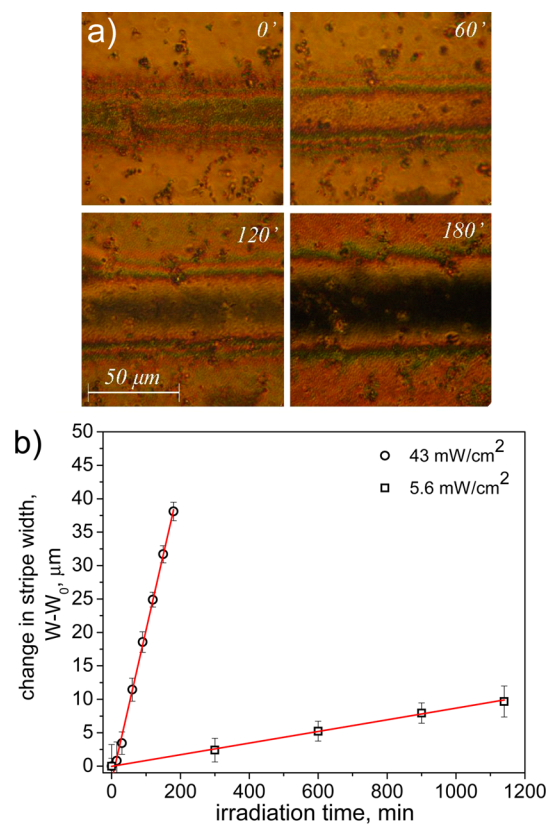


Figure 3. (a) Microscopic images between crossed polarizers for the same area of PAAzo6 sample, containing regions with mutually orthogonal LC director orientation; the images were taken at different times of irradiation (light intensity was 43 $\text{mW}\cdot\text{cm}^{-2}$, $\lambda = 546 \text{ nm}$).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

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

Another experimental confirmation of motion of domain boundaries can be found in the literature. A detailed experimental study of photo-orientation in an azobenzene-containing ionic self-assembly complex is reported by Zakrevskyy et al.⁶ 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

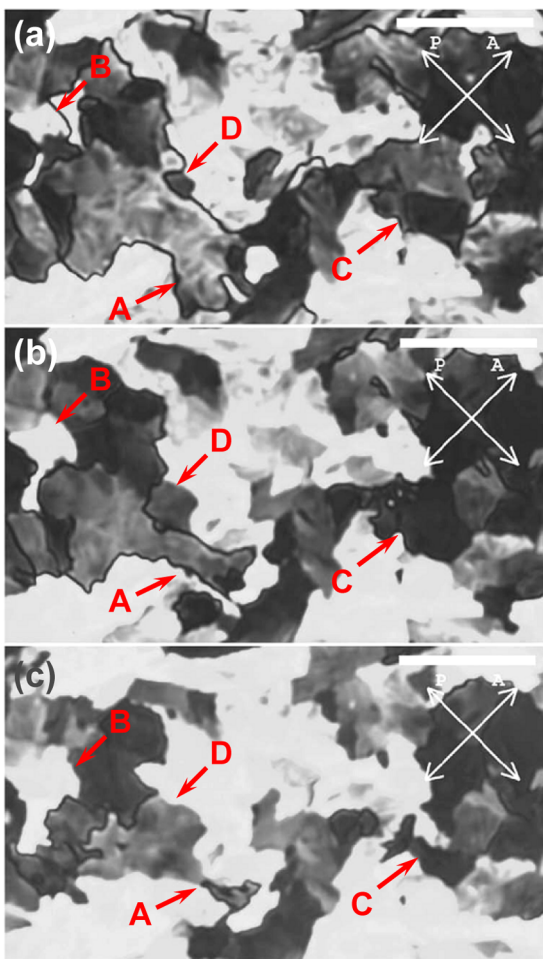


Figure 4. Microphotographs from ref 6 showing changes of microscopic textures of the film of the azobenzene-containing ionic self-assembly complex during its irradiation with polarized light: initial texture (a) and textures after exposure doses of 0.15 $\text{J}\cdot\text{cm}^{-2}$ (b) and 3 $\text{J}\cdot\text{cm}^{-2}$ (c). P and A indicate the directions of the transmission axes of the polarizer and analyzer; polarization of irradiating light is horizontal with respect to the picture; scale bar 10 μm . Reprinted from ref 6 with permission. Copyright 2007 American Physical Society.

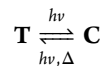
change during photo-orientation obtained in ref 6. It is seen that the domains marked as A and C diminish in the course of photo-orientation, whereas the domains B and D grow.

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 an azobenzene molecular fragment and the detailed consideration of the kinetics of photoisomerization of azobenzene derivatives within the 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 electronic³⁶ and vibrational³⁷ excitation proceeds within a 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 times of 10^{-11} – 10^{-9} s.^{38,39} 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 of 10^{-9} – 10^{-5} s in low molecular weight liquid crystals,³⁹ and can be much slower in liquid-crystalline polymers (up to 100–1000 s).^{40,41}

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 the 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 the kinetic equation of the isomerization reaction. The rate of isomerization in the approximation of the low optical density of the sample is given by the expression

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

where x_c is the molar fraction of the *cis* isomer, x_t is the molar fraction of the *trans* isomer, I is the light intensity expressed in $\text{Einstein}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $\bar{\epsilon}_t$ and $\bar{\epsilon}_c$ are the average extinction coefficients of *trans*- and *cis*-azobenzene units, φ_{tc} and φ_{ct} are quantum yields of *trans*-to-*cis* and *cis*-to-*trans* photoisomerization, and 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, and 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:

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

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

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

Table 1. Characteristics of Nematic Copolymer PAAzo6²²

photochemical characteristics		local order parameters ^a		model parameters	
φ_{tc}	0.16	$A_{0,0}^2$	0.78 ± 0.02	ξ	0.066 ± 0.004
φ_{ct}	0.66	$A_{0,0}^4$	0.506 ± 0.010	κ	8×10^{-4}
$\bar{\varepsilon}_t$	$100 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$	$A_{0,0}^6$	0.214 ± 0.015	τ_{ph}	0.157 min
$\bar{\varepsilon}_c$	$344 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$	$A_{0,0}^8$	0.065 ± 0.006	B'	$2.2 \mu\text{m}/\text{min}$
k_{ct}	$5.1 \times 10^{-3} \text{ min}^{-1}$			R_0	$2 \mu\text{m}$
$d_t p_t$	0.576 ± 0.016			β	0.1727
$d_c p_c$	0.034 ± 0.017				

^aLocal order parameters are taken as the corresponding values for the most ordered sample of PAAzo6 after prolonged (32 h) photo-orientation.

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

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

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

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 photo-isomerization 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 work²² 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 the 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:

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

where $\varepsilon_{||}$ and ε_{\perp} are components of the molecular extinction coefficient tensor and χ is an angle between the 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 the local orientation distribution function $\rho_L(\beta)$, defined as the number density of molecules oriented at angle β between the

domain director and the axis of the molecule extinction coefficient tensor. As shown in Appendix A to ref 22, the absorbance coefficient averaged over the 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 θ in expression 6 is the angle between the domain director and the electric field vector of light, $\bar{\varepsilon} = (\varepsilon_{||} + 2\varepsilon_{\perp})/3$ is an average extinction coefficient, $d = (\varepsilon_{||} - \varepsilon_{\perp})/3\bar{\varepsilon}$ is molecular dichroism, and 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. The 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 the 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 ξ and κ 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 expressions 8 and 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 and d_c and p_t and 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 the photoisomerization process for a test nematic polymer PAAzo6 were measured experimentally in our previous work.²² These values are listed in Table 1 (columns 1 and 2). By substituting these values into eq 10, one can obtain dependence of the photostationary concentration of *cis*-azobenzene units on domain orientation (Figure 5, straight line). It can be seen that

the content of *cis*-azobenzene fragments differs significantly in domains with different orientations.

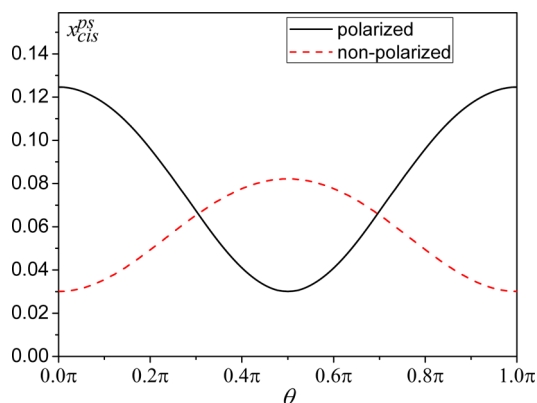


Figure 5. Dependence of photostationary mole fraction of *cis*-azobenzene units on domain orientation upon irradiation with polarized (straight line) and non-polarized (dashed line) light ($\lambda = 546$ nm).

The photo-orientation upon the irradiation with a parallel beam of non-polarized light is often considered experimentally.^{22,43,44} Under these conditions, the electric field vector of the light wave is distributed in the plane perpendicular to the 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 θ is an angle between light propagation direction and domain director.

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

$$x_c^{ps}(\theta) = \frac{\xi(1 - d \cdot p \cdot P_2(\cos \theta))}{\xi(1 - d \cdot p \cdot P_2(\cos \theta)) + (1 - \xi - \kappa)(1 - d \cdot p \cdot P_2(\cos \theta)) + \kappa} \quad (12)$$

The corresponding dependence calculated using parameters from Table 1 is plotted in Figure 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 a certain orientation in this case is equal to $N \sin \theta d\theta$, where $2N$ is the total number of domains and θ is the angle between the 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 θ_1 , and to the other side the director is oriented at an angle θ_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

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

It is assumed here that the domains are characterized on 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 the contact area of domains θ_1 and θ_2 in the total surface area of domains θ_1 is equal to the fraction of surface area of domains θ_2 in the 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 the 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 the molar Gibbs energy of the liquid-crystalline phase in domains with *cis* isomer fraction $x_c(\theta)$, and 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 θ :

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

According to the hypothesis stated in section C, the molar free energy of domain is determined by the 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, and difference in effective volumes of isomers.^{27,28,42,45} 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 α 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 the cases of light intensities of 43 and 5.6 mW/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 a large content of *cis*-azobenzene units into domain B with a low content of *cis*-azobenzene units leads to a 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 a time equal to the time of establishment of the 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 (eq 19) can be resolved numerically. The following dimensionless variables and parameters are appropriate for simplification of numerical integration:

$$\tau = (I \ln 10 \varphi_{tc} \bar{\epsilon}_t + I \ln 10 \varphi_{ct} \bar{\epsilon}_c + k_{ct}) t = t / \tau_{ph} \quad (20)$$

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

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

With the use of these notations, eq 19 is rewritten as follows:

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

The characteristics measured experimentally in our previous work²² are suitable for independent determination of values of model parameters. The obtained values are summarized in Table 1 (columns 5 and 6). In the experimental conditions,²² 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 eq 23 in this case. Since photoalignment 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 $\rho_D(\theta)$ (Figure 6a) can be used to obtain theoretical predictions for all characteristics of photo-orientation: experimentally observed order parameters, domain sizes, and values of absorbance. The experimentally

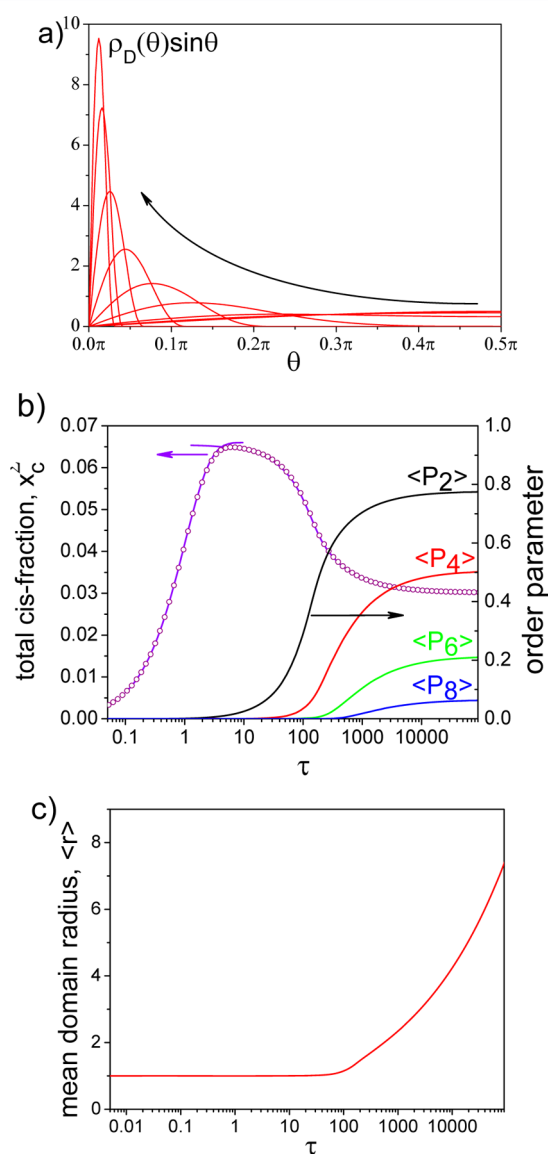


Figure 6. Modeling of photo-orientation upon the action of non-polarized light by eq 23 with experimentally measured parameters (Table 1): (a) evolution of the distribution function of domain orientations; (b) kinetics of the change of orientation order parameters (right-hand scale) and total cis isomer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

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 ref 22 with the spin probe technique are listed in Table 1 (columns 3 and 4). Figure 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 Figure 6c. The overall photostationary concentration of *cis*-azobenzene within the sample is calculated using the following expression:

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

The light absorbance is described by the expression

$$D(t) = \int ((1 - x_c(\theta, t))\epsilon_c(\theta) + x_c(\theta, t)\epsilon_c(\theta)) l c_0 \rho_D(\theta, t) \sin \theta \, d\theta \quad (28)$$

Figure 6b (left-hand scale, lines) shows the kinetic curve of the 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 the *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 (2-fold) 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.

The numerical results presented in Figure 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 Figure 7 with experimental results.²² Figure 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 Figure 7b. Figure 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

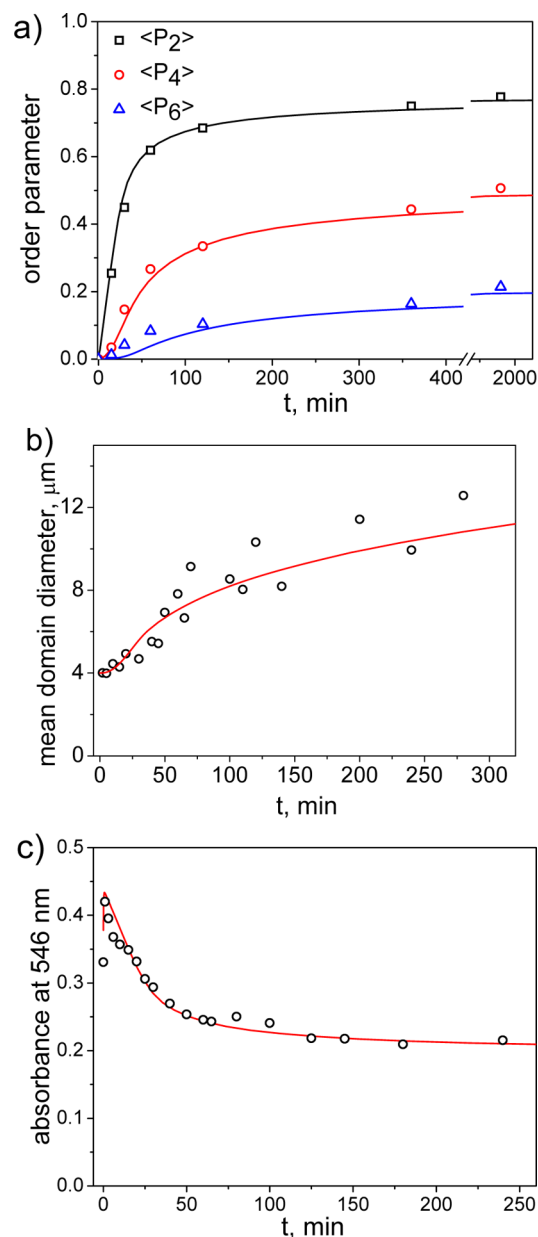


Figure 7. Comparison of predictions of model 23 with experimental measurements²² for photo-orientation of PAAzo6: (a) kinetics of orientation order parameters; (b) kinetics of mean domain size change; (c) kinetics of absorbance change at irradiation wavelength ($\lambda = 546$ nm).

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 interdomain boundary in a nematic material. Despite this, modeling results presented in Figure 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 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 Supporting Information, the rate of cis fraction change is determined by the expression:

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

The first two terms in eq 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 θ as a result of the accession of material from domains oriented at an angle θ' . Equations 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 by using photostationary values of $x_c(\theta)$. In Figure 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 reorientation of initially ordered material can also be rationalized in the framework of our model. Reorientation 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 photoinduced movement of the 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) Chemical structure and reactivity of the isomers, their aggregation, and the polymer free volume are taken into account through the values of quantum yields, extinction coefficients, and optical anisotropies of the isomers, which were measured in separate experiments.
- (2) Molecular shapes, intermolecular interaction, and its change upon isomerization determine the thermodynamic driving force for the photo-orientation process; these factors influence the kinetics of photo-orientation through the experimentally determined value of B' .
- (3) Rotation mobility of mesogenic units and the rate of the establishment of photostationary state also influence the rate of photoisomerization through the value of B' .

- (4) Thermal history, annealing, and aging of the polymer on photo-orientation lead to the modification of LC domain sizes,⁶ and thus are incorporated in our model.

All parameters explicitly included in our model were measured or estimated from independent experiments for azobenzene-containing nematic polymer. The photo-orientation characteristics calculated with use of the proposed model and the experimental findings are in good quantitative agreement.

■ ASSOCIATED CONTENT

Supporting Information

A detailed derivation of eq 29. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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