Direct Microscopic Observation of Domain Rearrangement Mechanism of Photo-Orientation Process in Azobenzene-Containing Materials

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S *Supporting Information*

ABSTRACT: The evolution of the domain structure of two azobenzene-containing materials during irradiation with polarized light was monitored using polarized optical microscopy with additional λ-waveplate for discerning the domains oriented parallel and perpendicular to irradiating light polarization. It is shown that the process of photo-orientation consists in growth of perpendicularly oriented domains and diminishing of parallel domains via the movement of domain boundaries. These data confirm the mechanism of photo-orientation via domain structure rearrangement.

photo-orientation by microstructure rearrangement
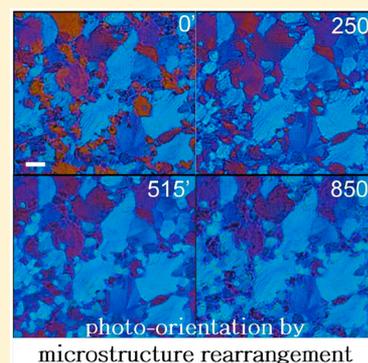
Light-induced orientation has been observed for numerous azobenzene-containing materials, including polymers,[1−4] liquid crystals,[5,6] molecular crystals,[7] and hydrogen- and halogen-bonded complexes.[8] This phenomenon impels the development of new smart materials, holographic media, devices for information storage, and so on. However, the mechanism of photo-orientation is still a debated question in the literature.[9−13] In 2013, we proposed a microscopic mechanism of photo-orientation,[14] formulated on the basis of a detailed experimental study of photo-orientation in liquid-crystalline azobenzene-containing polymer.[15] The idea behind this mechanism is as follows. It is known that azobenzene-containing materials, such as polymers, liquid crystals, and molecular crystals, are not homogeneous but rather consist of microscopic regions with different orientations. These regions, which are often called "domains", can often be observed by means of polarization microscopy. Upon the irradiation with light, photochemical isomerization process takes place in the material. Because of anisotropic light absorption of azobenzene moieties, the extent of photoisomerization (i. e., the fractions of trans and cis isomers) depends on the orientation of the domain with respect to the electric vector of the irradiating light. It is known that *cis*-azobenzene moiety is nonmesogenic[16,17] and therefore it disrupts liquid-crystalline or crystalline order in the domain, where its concentration is high. The domains oriented parallel to the electric vector of the irradiating light contain higher photostationary concentration of *cis*-azobenzene moieties and therefore they become less stable than perpendicular domains. Because of the difference in domain stability, the reorientation of the material in the vicinity of the domain borders takes place. As a result of this process the more stable perpendicular domains with lower amount of

cis-azobenzene grow at the expense of the less stable parallel ones. Macroscopically, this leads to preferential orientation of the material perpendicular to the electric field of light.

In our previous work we have shown that the described mechanism is in accordance with the experimental kinetic observations for photo-orientation of azobenzene-containing polymer.[14] In the present work we provide the direct microscopic observation of domain rearrangement in two low-molecular-weight azobenzene-containing materials. Chemical structures of the studied materials are shown in Figure 1. At room temperature, at which the experiments were performed in this work, substance I is in the crystalline and substance II is in the smectic phase.

The optical absorbance spectra of the two materials under study are illustrated in Figure 2. It is seen that the spectrum of substance I in solution is characterized by two principal bands, the π−π* band centered at 365 nm and the n−π* band with the maximum around 440 nm. These bands are characteristic of azobenzene derivatives.[18] In material II the π−π* band is shifted to longer wavelength and is overlapped with the n−π* band. This phenomenon is well known for azobenzene substances with a donor substituent in one benzene ring and an acceptor substituent in another one (push−pull substitution).[18,19] Spin-coated films of both substances (Figure 2, red lines) demonstrate the shift of the π−π* band to shorter wavelength compared with the spectra in solution, which may result from chromophore aggregation and polarity effects. It is
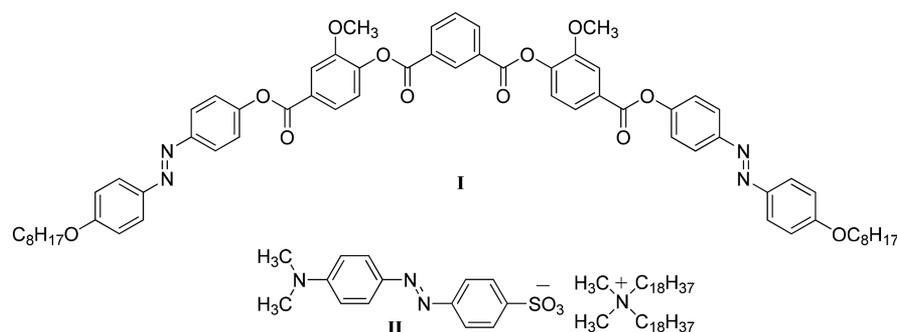
Figure 1. Chemical structures of azobenzene-containing materials used in the present work.
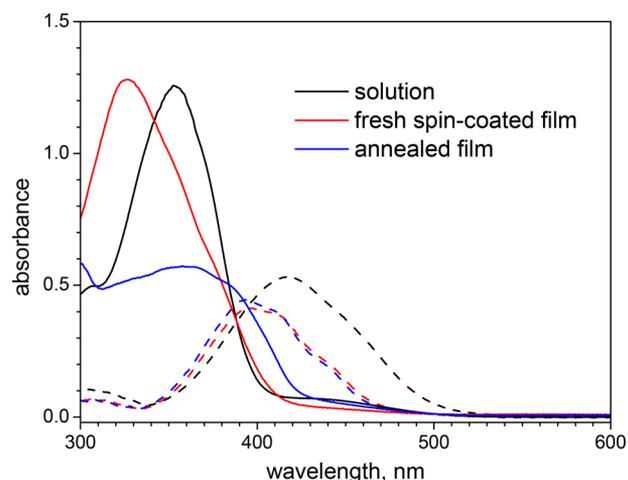
Figure 2. Absorption spectra of materials I (solid lines) and II (dashed lines) in solution (black lines), in the spin-coated film as freshly prepared (red lines), and after annealing the film for 20 min at 100 °C (blue lines).

Figure 3. (a) Optical scheme of polarization optical microscopy with λ-waveplate; P1 and P2 denote polarizer and analyzer. (b) Microphotograph of the same area of material I made with (right panel) and without (left panel) the λ-waveplate.

seen that the annealing of the spin-coated film of material I leads to a significant change of the absorption spectrum (Figure 2, blue solid line), namely, the shift of the $\pi-\pi^*$ band to the longer wavelength, which indicates the change of the aggregation state of the chromophores as a result of the annealing. It is known in the literature[1,5] that the annealing of azobenzene-containing materials leads to the change of the sample morphology and affects the photo-orientation rate. For this reason, the thermal history of samples in the present work was unified for all of the experiments. Prior to irradiation, the samples were annealed for 20 min at 100 °C. More detailed information on the absorption spectra of the studied materials is given in the Supporting Information (Figures S1, S4, and S6).

The domain structure of the material in the course of photo-orientation was observed using optical microscopy in polarized light. Along with conventional microscopic observation of the sample between the crossed polarizers, the imaging with additional phase retardation plate between the polarizers was used (Figure 3a). The 550 nm λ-waveplate was used as a phase retarder. The slow axis of the waveplate was oriented at 45° to transmission axes of polarizer and analyzer (denoted P1 and P2 in Figure 3a). Because of the additional phase difference introduced by the waveplate, the regions of material with mutually perpendicular orientations appear as having different colors between the crossed polarizers.[20] It is illustrated in Figure 3b, where the experimentally obtained microscopic images of the same region of the sample of material I with and without the waveplate are presented. It is well seen there that
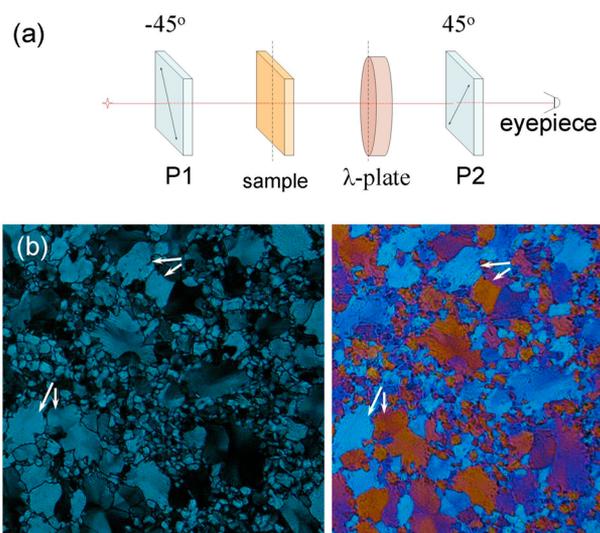
some domains that have the same appearance in the conventional polarization optical microscopy (marked by arrows) have mutually perpendicular alignment, which is easily discerned with the use of the λ-waveplate.

Figure 4 illustrates kinetics of polarized absorbance change in the course of irradiation of the samples of I (Figure 4a) and II (Figure 4b) with linearly polarized light. It is seen that the irradiation results in the rise of the absorbance in perpendicular polarization and the decrease in absorbance in parallel polarization. Thus the photo-orientation process is observed. It is seen that for material I the photo-orientation proceeds much slower than that for material II. The reason for this is obviously that the material I is in the crystalline phase, where molecular mobility is significantly lower than that in the liquid-crystalline smectic phase of material II.

The insets in Figure 4 show the initial moments of irradiation. It is seen that the decrease in absorbance is observed in both polarizations, which is the result of reaching the photostationary state of trans−cis photoisomerization of azobenzene moieties.[19] It is seen that the amplitude of the absorbance change is higher in polarization parallel to that of irradiating light. This is consistent with the fact that the photostationary concentration of *cis*-azobenzene moieties is higher in domains oriented parallel to irradiating light polarization[14,21] due to different orientations of transition dipole moments in *trans*- and *cis*-azobenzene fragments. As it is
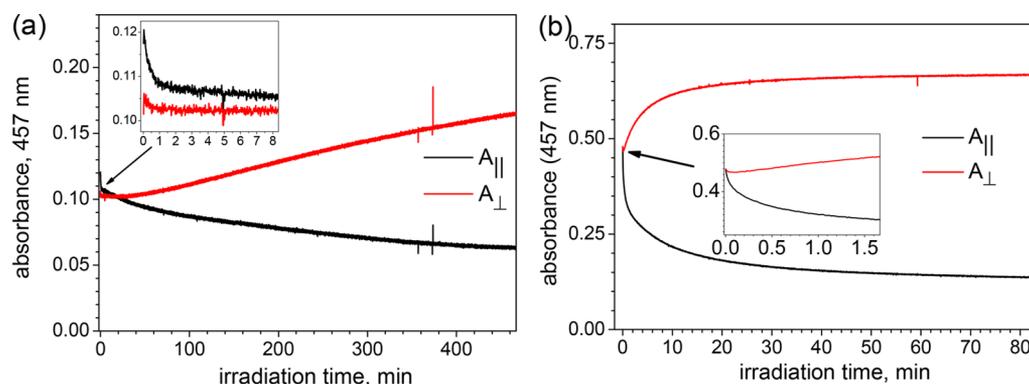
Figure 4. Kinetics of polarized absorbance change upon irradiation with linearly polarized light (457 nm) of materials I (a) and II (b). The insets display the initial parts of kinetic curves.
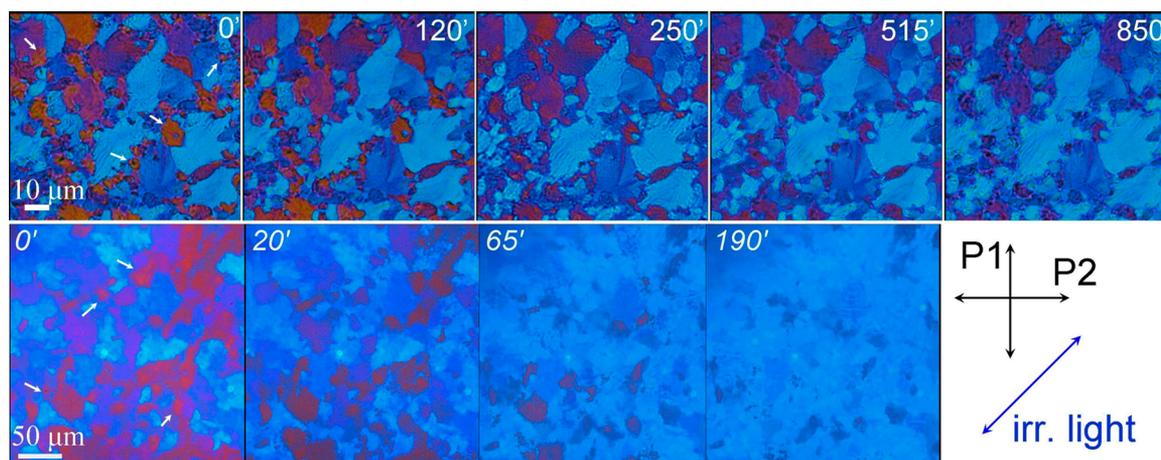
Figure 5. Microscopic images of materials I (upper panel) and II (lower panel) in the course of photo-orientation. The times of irradiation in minutes are indicated in each image. The images were obtained by polarization optical microscopy in crossed polarizers with λ-waveplate. White arrows indicate domains, which diminish and vanish in the course of irradiation.

well known from literature, the transition dipole moment of *trans*-azobenzene fragments is directed along the axis of the azobenzene fragment, whereas for *cis*-azobenzene fragments the transition dipole moment tends to lie in the plane perpendicular to N−N bond.[22,23]

The microphotographs of the same regions of materials I and II at different moments of irradiation are shown in Figure 5. These photographs were obtained using the additional waveplate in microscope optical path, as described in the Experimental Details. Here the areas with different colors correspond to domains with different orientations: the orange- or pink-colored regions correspond to parallel oriented domains, light-blue shaded regions correspond to perpendicularly oriented ones, and the intermediate colors correspond to intermediate orientations of domains. The photographs in Figure 5 show that the process of photo-orientation is accompanied by the change of shape and size of the microscopic domains. The parallel oriented domains, which markedly change their shape and size during irradiation, are shown in Figure 5 with white arrows.

Thus the experiment shows that the photoinduced orientation of the investigated materials is accompanied by the change in their domain structure. Therefore, the model of photo-orientation developed in ref 14 is suitable for describing photo-orientation of these materials. The important kinetic characteristic of the photo-orientation process is the speed of

the domain boundary movement per unit difference in *cis*-azobenzene concentration in two domains. This parameter can be estimated from the microphotographs in Figure 4. From measuring the sizes of a number of parallel domains in Figure 5 changing in the course of photo-orientation, the speed of domain boundary movement can be estimated as ∼0.005 μm/min for material I and ∼0.2 μm/min for material II. The difference in *cis*-azobenzene molar concentration in parallel and perpendicular domains can be estimated from the initial regions of the kinetic curves shown in Figure 3 to be ∼0.12 mol·L^{-1} for material I and ∼0.16 mol·L^{-1} for material II. These estimates were obtained under an assumption that the extinction coefficient of *trans*-azobenzene units is much higher than that of *cis*-azobenzene units at the irradiation wavelength. Thus the speed of the domain boundary movement per unit difference in *cis*-azobenzene concentration is estimated as ∼0.04 μm·min^{-1}·L·mol^{-1} for material I and ∼1.2 μm·min^{-1}·L·mol^{-1} for material II. These values should be regarded only as estimates; the more accurate values require the knowledge of kinetic parameters of photoisomerization of the investigated materials.

The experiments carried out in the present work provide direct evidence that the photo-orientation of two low-molecular-weight azobenzene-containing materials proceeds via the change of their microscopic domain structure. This result is contrary to the widely assumed mechanism of molecular turns in the cycles of trans−cis−trans photo-

isomerizations of azobenzene moieties.[9,11] The experimentally observed nonuniform orientation of such materials and its evolution in the course of light irradiation should be taken into account for the theoretical modeling of photo-orientation process. An example of such a model was developed by the present authors in ref 14.

EXPERIMENTAL DETAILS

Chemical structures of the studied materials are shown in Figure 1. Bis-azobenzene substance I was synthesized in the group of Prof. A. Bubnov.[24] Phase-transition temperatures for this material are 174 °C (crystal to nematic) and 196 °C (nematic to isotropic), which was measured with differential scanning calorimetry (DSC) and temperature-dependent polarization optical microscopy.[24] Photoisomerization was monitored by optical absorbance spectroscopy. The absorption spectrum of material I in chloroform solution and in the solid state is given in the Supporting Information (Figures S1 and S4). The spectral changes upon photoisomerization in solution (Supporting Information, Figure S2) are consistent with the literature data on photoisomerization of azobenzene derivatives.[19] It is worth noticing that because material I is bis-azobenzene, the successive photoisomerization of the two azobenzene fragments inside one molecule may take place during irradiation. However, under the irradiation conditions of the present work, the fraction of cis-azobenzene fragments is estimated as 6%, which gives the negligibly small fraction of Z,Z-isomers of 0.34% (assuming independent photoisomerization of each azobenzene fragment).

Ionic self-assembly salt II was synthesized by the procedure described in ref 5 for the synthesis of a similar complex. Water solutions of methyl orange and dimethyldioctadecylammonium bromide (Aldrich) were mixed at the stoichiometric ratio. The precipitated solid was vacuum-filtered and dried in vacuo (10^{-2} Torr, 1 day). Phase-transition temperatures of this material were measured by polarization optical microscopy. At room temperature the complex forms smectic phase similar to that of ethyl orange−dimethyldidodecyl ammonium bromide complex described in ref 5. At 118.5 °C the substance transforms into another smectic phase, the transition being accompanied by strong enlargement of liquid-crystalline domains. At 125 °C the substance II transforms into isotropic state. This transition is accompanied by rupture of a thin spin-coated film and the formation of droplets, that is, dewetting. The absorbance spectrum of material II in chloroform solution and in the solid state is given in the Supporting Information (Figures S1 and S6). Figure S5 illustrates the spectral changes upon photoisomerization and thermal cis−trans isomerization in the solid film.

In the absence of irradiation, thermal cis−trans isomerization takes place for both materials. The characteristic time of thermal cis−trans isomerization of material I is 675 min in chloroform solution (Figure S3) and ca. 100 h in the solid film. The characteristic time of thermal cis−trans isomerization for material II in the solid film is ca. 4 min (Figure S5). Thus for both materials under the conditions of the experiments described in the present paper, characteristic times of thermal isomerization are much longer than the times of reaching the photoisomerization stationary state (1 min for material I and 10 s for material II).

At room temperature, at which the experiments were carried out in this work, substance I is in the crystalline and substance II is in the smectic phase. It has been checked that at the starting moments of irradiation (1 min), after the steady state of trans−cis photoisomerization is reached, no visible change in microscopic textures of the samples are observed, which is the indication that the phase states of the materials remain the same under the conditions of the experiments carried out in the present work.

The samples of thin films of azobenzene-containing materials on glass slides were prepared by spin-coating from chloroform solutions (10−20 mg/mL, rotation speed 1000 rotations per minute). Sample thicknesses were estimated by optical absorption spectroscopy and were about 300−500 nm. Prior to irradiation, the samples were annealed for 20 min at 100 °C to ensure the identical thermal history all the samples.

To probe the possible anisotropy of material orientation with respect to the film surface, polarized absorbance spectra were recorded under the conditions of oblique incidence of spectrometer probe light on the film. The details of the technique are reported elsewhere.[15] The experimentally obtained principal components of absorbance tensor are presented in the Supporting Information (Figure S8). For material I, the freshly prepared spin-coated films show slight homeotropic orientation, which turns into planar preferential orientation upon annealing. For material II, both fresh and annealed films were found to be isotropic within the experimental accuracy.

For photo-orientation measurements, the irradiation of the samples was performed with linearly polarized defocused diode laser beam of wavelength 457 nm. The light intensity was 50 mW/cm^2. Every 1 s of irradiation, the light intensity was decreased by ∼100 times, and sample transmission was probed in polarizations parallel and perpendicular to that of the irradiating light. The probing took ∼0.25 s. Polarization of the probe light was controlled by electro-optical LC cell equipped with a polarizer. By this means, the kinetics of light absorption in the process of photo-orientation was measured.

Microscope Axioscope 40Pol (Carl Zeiss) equipped with CCD camera was used for microscopic observations. The 550 nm quartz waveplate was used between the crossed polarizers as the first-order phase retarder.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b00294.

> Additional information (absorbance spectra, kinetic curves) with respect to the materials discussed in the present work (PDF)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Bobrovsky, A.; Ryabchun, A.; Medvedev, A.; Shibaev, V. Ordering Phenomena and Photoorientation Processes in Photochromic Thin Films of LC Chiral Azobenzene-Containing Polymer Systems. *J. Photochem. Photobiol., A* **2009**, *206*, 46−52.

(2) Buffeteau, T.; Labarthet, F. L.; Pézolet, M.; Sourisseau, C. Dynamics of Photoinduced Orientation of Nonpolar Azobenzene Groups in Polymer Films. Characterization of the Cis Isomers by Visible and FTIR Spectroscopies. *Macromolecules* **2001**, *34*, 7514−7521.

(3) Stumpe, J.; Lasker, L.; Fischer, T.; Rutloh, M.; Kostromin, S.; Ruhmann, R. Photo-Orientation in Amorphous and Aligned Films of Photochromic Liquid Crystalline Polymers. *Thin Solid Films* **1996**, *284−285*, 252−256.

(4) Rosenhauer, R.; Fischer, T.; Stumpe, J. Light-induced Anisotropy of Stilbene Containing LC Polymers and Its Thermal Development by Self-organization. *Proc. SPIE* **2003**, 169−182.

(5) Zakrevskyy, Y.; Stumpe, J.; Smarsly, B.; Faul, C. F. Photo-induction of Optical Anisotropy in an Azobenzene-Containing Ionic Self-Assembly Liquid-Crystalline Material. *Phys. Rev. E* **2007**, *75*, 031703.

(6) Stracke, A.; Wendorff, J. H.; Goldmann, D.; Janietz, D. Optical Storage in a Smectic Mesophase: Thermal Amplification of Light-induced Chromophore Orientations and Surface Relief Gratings. *Liq. Cryst.* **2000**, *27*, 1049−1057.

(7) Chigrinov, V.; Prudnikova, E.; Kozenkov, V.; Kwok, H.; Akiyama, H.; Kawara, T.; Takada, H.; Takatsu, H. Synthesis and Properties of Azo Dye Aligning Layers for Liquid Crystal Cells. *Liq. Cryst.* **2002**, *29*, 1321−1327.

(8) Medvedev, A. V.; Barmatov, E. B.; Medvedev, A. S.; Shibaev, V. P.; Ivanov, S. A.; Kozlovsky, M. V.; Stumpe, J. Phase Behavior and Photooptical Properties of Liquid Crystalline Functionalized Copolymers with Low-Molecular-Mass Dopants Stabilized by Hydrogen Bonds. *Macromolecules* **2005**, *38*, 2223−2229.

(9) Kiselev, A. Kinetics of Photoinduced Anisotropy in Azopolymers: Models and Mechanisms. *J. Phys.: Condens. Matter* **2002**, *14*, 13417−13428.

(10) Yaroshchuk, O.; Kiselev, A.; Zakrevskyy, Y.; Bidna, T.; Kelly, J.; Chien, L. C.; Lindau, J. Photoinduced Three-dimensional Orientational Order in Side Chain Liquid Crystalline Azopolymers. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2003**, *68*, 011803.

(11) Pedersen, T. G.; Johansen, P. M.; Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. Theoretical Model of Photoinduced Anisotropy in Liquid-Crystalline Azobenzene Side-Chain Polyesters. *J. Opt. Soc. Am. B* **1998**, *15*, 1120−1129.

(12) Chigrinov, V.; Pikin, S.; Verevochnikov, A.; Kozenkov, V.; Khazimullin, M.; Ho, J.; Huang, D.; Kwok, H.-S. Diffusion Model of Photoaligning in Azo-Dye Layers. *Phys. Rev. E* **2004**, *69*, 061713.

(13) Sekkat, Z.; Ishitobi, H.; Yasumatsu, D.; Kawata, S. Photo-Orientation Movement of Photoisomerizable Chromophores: Quantifying Analytical Theory and Application to Spectrally Overlapping and Distinguishable Isomers. *Proc. SPIE* **2000**, *4106*, 133−145.

(14) Bogdanov, A.; Vorobiev, A. Photo-Orientation of Azobenzene-containing Liquid-Crystalline Materials by Means of Domain Structure Rearrangement. *J. Phys. Chem. B* **2013**, *117*, 13936−13945.

(15) Bogdanov, A.; Vorobiev, A. ESR and Optical Study of Photoorientation in Azobenzene-Containing Liquid-Crystalline Polymer. *J. Phys. Chem. B* **2013**, *117*, 12328−12338.

(16) Ikeda, T.; Tsutsumi, O. Optical Switching and Image Storage by Means of Azobenzene Liquid-Crystal Films. *Science* **1995**, *268*, 1873−1875.

(17) Sobolewska, A.; Zawada, J.; Bartkiewicz, S.; Galewski, Z. Mechanism of Photochemical Phase Transition of Single-Component Phototropic Liquid Crystals Studied by Means of Holographic Grating Recording. *J. Phys. Chem. C* **2013**, *117*, 10051−10058.

(18) Rau, H. Spectroscopic properties of organic azo compounds. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 224−235.

(19) Rau, H. Azo Compounds. In *Photochromism. Molecules and Systems.*; Durr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 2003; pp 165−192.

(20) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North Holland Pub. Co, 1977.

(21) Janossy, I.; Szabados, L. Photoisomerization of Azo-dyes in Nematic Liquid Crystals. *J. Nonlinear Opt. Phys. Mater.* **1998**, *7*, 539−551.

(22) Beveridge, D. L.; Jaffe, H. H. The Electronic Structure and Spectra of cis- and trans-Azobenzene. *J. Am. Chem. Soc.* **1966**, *88*, 1948−1953.

(23) Fliegl, H.; Köhn, A.; Hättig, C.; Ahlrichs, R. Ab Initio Calculation of the Vibrational and Electronic Spectra of trans- and cis-Azobenzene. *J. Am. Chem. Soc.* **2003**, *125*, 9821−9827.

(24) Bobrovsky, A.; Shibaev, V.; Hamplová, V.; Bubnov, A.; Novotná, V.; Kašpar, M.; Piryazev, A.; Anokhin, D.; Ivanov, D. Photo-Optical Properties of Amorphous and Crystalline Films of Azobenzene-Containing Photochromes with Bent-Shaped Molecular Structure. *J. Photochem. Photobiol., A* **2016**, *316*, 75−87.