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Light-induced changes of optical and electrical properties in bent-core azo compounds


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We have studied the optical and electrical properties of two bent-core substances with an azo linkage in their cores. Pump-probe laser studies, direct textural observations, and spectrophotometric recordings show an initial decrease of light transmission, which at larger light intensities (~1 mW/mm²) is followed by a bleaching. Simultaneously the electrical properties (electric conductivity, antiferroelectric polarization, switching threshold, and switching time) decreased monotonically with increasing light intensities. The monotonic decrease of electrical properties indicates that the darkening and bleaching have the same origin, namely, the photochemical isomerization of the azo linkage from the trans to the cis isomer. The material with cis isomer has a lower clearing point and phase separates from the trans-rich domains. Initially the size of the separated isotropic domains is below the visible range, which causes increased scattering. As the size of the isotropic domains increase the scattering disappears and the transmittance becomes the average of the transmittances in the polar tilted smectic and isotropic phases.

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INTRODUCTION

In the last several years it became evident that bent-core (banana) smectics have a number of unique properties. The bent shape of the molecules results in polar packing [1], which together with a director tilt gives rise to layer chirality that does not require chirality on the molecular level [2]. These smectic materials mainly form antiferroelectric [3] states with electric polarizations in the range of 500 nC/cm². They show extremely rich behavior under electric fields: the morphology can be extended to light sensitivity by doping with dyes or incorporating azo linkage [4]. This rich morphology can be extended to light sensitivity by doping with dyes or incorporating azo linkage(s) into the bent-shape molecules [5,6]. Recently, preliminary observations of light-induced reversible changes of the electrical properties were reported [7] on a bent-core material (AB-12) with alky terminal chains consisting of five aromatic rings and containing an azo linkage only in one arm.

In this paper we present detailed optical and electrical studies on AB-12 and on a similar bent-core azo material (AB-10), where previously no photoresponse was observed [7]. We show that AB-10 is also photosensitive at larger light intensities, which, however, still can be reached with the microscope light, enabling us to trace the light-induced structural effects by simple microscopy. Based on these measurements we propose a model to describe the structural changes induced by light.

EXPERIMENT

The molecular structures and phase sequences of AB-10 and AB-12 are shown in Fig. 1. They differ only in the length of one of the alkyl chains and both form antiferroelectric polar tilted smectic (Sm-C₃) phase in a very similar temperature range: between 110 and 130 °C. The light-induced changes in their optical properties were studied either using a microscope, or by a pump-probe laser setup. In the microscope (Olympus BX60), the light source was the microscope lamp itself (HLX 64623 from OSRAM 100 W halogen lamp). The optical response was detected with an Ocean Optics spectrophotometer, replacing the microscope eyepiece by an optical fiber that collected the transmitted light. No polarizer was inserted into the microscope. The change of transmission was measured at a selected wavelength as a function of the time, with an acquisition time of 30 ms. Additionally, the variation of the texture was monitored with a charge-coupled device camera mounted on the microscope.

In the laser experiments the pump and the probe beams were provided by two argon-ion lasers tuned to the wavelength 488 nm, which falls into the absorption band of the compounds studied. The probe beam had very low intensity to avoid its influence on the transmission measurements. The changes of transmission of the probe as a function of the pump intensity were detected.

Light- and external-voltage-induced electric currents were measured when the sample was placed in the microscope. The electric current has different sources. First, there is a current carried by the ions inherently present in the material.

![Molecular structures and phase sequences of the studied materials](image)
The number of charges can be increased by an optical field, which can ionize the liquid crystal molecules and can also inject charges from the electrodes through the photoeffect. The excess current due to light is considered as a photocurrent. In addition, the change of the electric polarization ($P$) in the system gives rise to a transient current $dP/dt$ (polarization current). The polarization current is especially large when the antiferroelectric-ferroelectric transition takes place, as in this case a spontaneous polarization is formed.

The spontaneous polarization was followed by the standard method, detecting the current generated by a triangular voltage. The dc resistance was measured by a multimeter HP34401A.

RESULTS

In the isotropic phase the variation of the transmission showed the well-known characteristics of trans-cis photoisomerization [15]. As our materials in the isotropic phase have relatively low viscosity (<10 Pas), photoinduced orientational ordering of the molecules [8,9] can be neglected. The transmission decreases for both materials up to about 20–25% when the samples are illuminated by the laser light with intensity up to 15 mW/mm$^2$. The time dependences of the transmissions after turning the light on and off are shown in Fig. 2(a), whereas the pump intensity dependences of the probe transmissions are plotted in Fig. 2(b) for the two compounds. Spectrophotometric measurements carried out in the microscope showed no change in the transmittance for wavelengths outside the absorption band. The change of transmission in the absorption band therefore can be attributed to the formation of cis isomers, which have a different absorption spectrum from trans isomers. The decrease of transmission indicates that the cis configuration has a higher absorption coefficient at 488 nm than the trans one. From the measurements alone it is not possible to determine the saturation cis concentration. One can estimate, however, the saturation intensity, which corresponds to the intensity where the concentration of the cis isomers is half of its saturated value [10]. From Fig. 2(a), we find that the saturation intensity at 488 nm is about 7 mW/mm$^2$ for both compounds. From the decay of the probe transmission change, observed after switching off the pump [see Fig. 2(a)], one can obtain the $\text{cis-trans}$ thermal back-relaxation time by measuring the time interval between 10% and 90% changes. We found that at 140 °C $\tau_{\text{cis-trans}}$ is 11.1 s for AB-12 and 12.3 s for AB-10, whereas $\tau_{\text{trans-cis}}$ is 7.5 s for AB-12 and 7.3 s for AB-10.

In the antiferroelectric Sm-$\text{CP}_4$ phase at low light intensities and at lower temperatures the laser illumination induced a decrease of the transmittance. For both materials the photodarkening is roughly three times in the Sm-$\text{CP}_4$ phase than in the isotropic fluid. In the laser experiments no polarization dependence was found in the probe transmission. Photodarkening was also observed with spectrophotometric recordings at wavelengths both inside and outside the absorption band; therefore it could be attributed to increased scattering rather than to increased absorption. In the microscope the darkening of the texture appeared uniformly over the whole illuminated area. At higher temperatures (a few degrees below the clearing point), or at high intensities, significant bleaching followed the initial decrease of transmittance. Under constant pump intensity of 0.9 mW/mm$^2$ the bleaching occurred above 124 °C for AB-12 as can be seen from the temperature dependence of the relative normalized transmittances in Fig. 3(a). Simultaneous textural observations clearly showed that the bleaching is due to the appearance of isotropic droplets within the Sm-$\text{CP}_4$ phase. With increasing light intensity or temperature, the droplets joined together forming large (10–50 µm size) isotropic regions with elongated Sm-$\text{CP}_4$ domains floating in the isotropic fluid. The isotropic droplets appeared only above some threshold light intensity with decreasing time intervals. At lower temperatures this threshold increased quickly (e.g., ~5 mW/mm$^2$ at 121 °C), as it can be seen on Fig. 3(b) for both materials. The time dependences of the transmitted light intensities and snapshots of the corresponding textures of 50 µm thick films are shown in Fig. 4.

The effect of the illumination was also tested in the ferroelectric state, which was generated by an electric field in thin (<10 µm) cells. We found that the basic effects (initial darkening, then bleaching at higher temperatures and higher intensities) were qualitatively the same in the ferroelectric and antiferroelectric states.

The light-induced changes of the electric properties were measured during illumination with the microscope light.

FIG. 2. Relative transmittances in the isotropic phases ($T = 140$ °C) of the two materials. (a) The transmittances after turning the light on and off, normalized to the transmittance of the unilluminated sample; (b) the pump intensity dependences of the relative normalized transmittance ($T_{\text{off}} - T_{\text{on}})/T_{\text{off}}$ of the probe beam.
Changes in the value of the spontaneous polarization, the switching threshold, the switching times, and the electric conductivity were detected. The polarization current curves recorded in both nonilluminated and illuminated samples are shown for AB-10 in Fig. 5. It can be seen that not only did the value of the spontaneous polarization (the integral areas below the current peaks) decrease, but also the threshold electric fields for switching between the antiferroelectric and ferroelectric states (determined from the peak positions). In Fig. 6 we have plotted the time dependences of the polarization and the transmittance of the AB-10 sample after the microscope light with integrated intensity of 9 mW/mm² was switched on. We see that the value of the electric polarization decreases monotonically in about 15 s from 350 to 200 nC/cm² at 121 °C. The simultaneous time dependence of the transmittance was more complicated: first the transmittance decreased quickly (in about 2 s); then it increased and became constant in about 10 s.

The temperature dependence of the equilibrium electric resistance of a 4 µm AB-12 cell is plotted in Fig. 7. In the smectic phase the resistance was smaller in the dark state, whereas it became larger in the isotropic state. Interestingly the resistance was smaller in the Sm-CPA phase than in the higher-temperature isotropic phase. The time dependences of

FIG. 5. Voltage dependence (triangular wave, f=23 Hz) of the polarization current at 121 °C of 4 µm sample of AB-10 measured in the nonilluminated sample, and under 9 mW/mm² white light illumination. The dashed lines indicate the voltages required for switching from the antiferroelectric state to ferroelectric and back from ferroelectric to antiferroelectric in the nonilluminated and illuminated samples.

FIG. 4. Time dependences of the transmitted light intensity outside of the absorption band (600 nm) of a 50 µm AB-12 cell at different temperatures in the antiferroelectric state (zero electric field applied). The sample is illuminated by the microscope white light (integrated intensity 9 mW/mm²). The pictures were taken by using attenuators between the sample and camera. The attenuation in case of picture (d) is much greater than in the other pictures.
FIG. 6. Simultaneous time dependence of the magnitude of the electric polarization and the transmittance of AB-10 at 121 °C. Starting at \( t=0 \) the sample is illuminated by the microscope light (integrated intensity of 9 mW/mm\(^2\)). The magnitude of the polarization was obtained by recording the time dependence of the polarization current in one period of 23 Hz triangular wave voltage, and transferring the data from the scope to the computer in 1 s interval. The magnitudes of the polarizations corresponding to the different times after the light was turned on were calculated after the measurement from the areas below the polarization peaks.

The resistance after turning the light on and off are shown in Fig. 7(b). It is seen that the resistance decreases (increases) abruptly, and then increases (decreases) gradually when the light is turned on (off). The relaxation times can be determined by fitting the resistance with the equations \( R(t) = R_{\text{steady}} \pm \Delta R e^{-t/\tau} \) for the bright and dark states, respectively. The fits shown with solid lines give that the relaxation time in the illuminated sample is \( \tau_{\text{on}}=5.9 \) s, and in the nonilluminated sample it is \( \tau_{\text{off}}=15.3 \) s. Interestingly the direction of the jumps is opposite to the steady state values, which are larger in the illuminated sample (see dashed line), in accordance with the steady state measurements shown in Fig. 7(a).

The resistance was determined from the electric current flowing under 1 V dc voltage applied on the electrodes. Accordingly, one can calculate that \( \Delta R=7 \times 10^5 \) \( \Omega \) change of the resistance corresponds to a transient photocurrent of about 0.8 nA. This value is about an order of magnitude larger than in azo-dye-doped liquid crystals [11].

**DISCUSSION**

First we consider possible explanations of the increase of scattering at low illumination levels. One possible explanation is that due to photoisomerization textural changes occur within the Sm-\( CP_A \) phase. Such light-induced transformations of the texture were observed in the past in various liquid crystalline systems. Folks et al. [12] detected light-induced layer undulations in a smectic-\( A \) phase containing an azo compound. Another example is the photoorientation effect in Langmuir-Blodgett films, studied, e.g., by Palto et al. [13]. The textural changes can straightforwardly result in increased scattering. An alternative explanation is that small, submicrometer size isotropic droplets form within the liquid crystalline phase (see below).

At higher light intensities the experiments clearly showed a light-induced phase separation between the antiferroelectric

FIG. 7. dc resistance of a 4 \( \mu \)m thick 0.25 cm\(^2\) area cell of AB-12. (a) Temperature dependence of nonilluminated and illuminated (integrated intensity of the microscope light 0.9 mW/mm\(^2\)) samples. Data were taken in heating with 1 °C/min rates. (b) Time dependence at 127 °C after the microscope light is switched on and off.

Sm-\( CP_A \) and isotropic fluid phases. The phase separation is not due to significant changes of the local temperature, which from the absorption spectrum published previously [7] can be estimated [14] to be less than 1.8 °C even at the highest light intensity, whereas we observed the phase separation even 10 °C below the clearing point. We conclude that the phase separation is due to trans-cis isomerization, i.e., partial conversion of the molecules from the stable trans to the metastable cis form. The mechanism behind this process is that the trans isomers usually have a more elongated shape than the V-shaped cis isomers; the latter isomer therefore decreases the stability of the liquid crystalline phases. As a consequence, photogeneration of the cis component lowers the phase transition temperatures. If a significant amount of cis isomers is created, the shift of the phase transition temperature may be sufficient to induce a phase transition. In our case the bent (banana-shape) molecules form closed packed smectic layers when the azo group is in the trans form. In the cis form the molecules have zigzag shape that—due to the asymmetric position of the azo group—is not compatible with the close packed smectic ordering (see Fig. 8). Such incompatibility causes phase separations between the isotropic fluid and the Sm-\( CP_A \) phase. Since the cis isomers are present in both phases, we can assume that the polar order is weaker in the illuminated smectic domains. This is schematically indicated in Fig. 8 with lighter background color than
in the well-ordered dark state indicated with darker background color.

The general condition for equilibrium between coexisting phases is that the chemical potential of the components should be equal in the isotropic and smectic phases. The actual physical processes leading to the equilibrium, however, are quite complicated, because the exciting light beam can induce transitions in both directions and ever, are quite complicated, because the exciting light beam should be equal in the isotropic and smectic phases. The observed transient behavior of the dc resistance can be attributed to the photogeneration of charges as the other two mechanisms take place on a much longer time scale than the sudden change in the measured resistance. The time dependence of the decay of the transient photocurrent was found to be similar to that for other azo-based materials \[11\], and may be explained by the recombination and diffusion of the photoinduced space charges. Because the material absorbs light there will be more charge generated around the electrode closer to the light source. This results in an internal field, which will be slowly screened out by the free ionic charges that are present in the material. When the light is switched off the photogenerated charges disappear leaving an opposite internal field inside which results in an increased resistance. Similar to the previous case this internal field will be again screened out slowly. The mobility of charges is different in the \textit{cis} and \textit{trans} states, explaining the larger relaxation time in the nonilluminated than in the illuminated samples. The observation that the electric conductivity is larger in the Sm-\textit{CP} \textsubscript{A} phase than in the isotropic fluid is not related to the presence of the azo unit, because we consistently observed it for other bent-core Sm-\textit{CP} materials without azo linkage. We think it maybe connected to the tighter and more polar packing of the molecules in the Sm-\textit{CP} \textsubscript{A} phase, which may result in some overlapping of the \textit{\pi} orbitals of the adjacent molecular cores. The decrease of the resistance upon illumination in the isotropic phase indicates that the \textit{cis} configuration has a larger electric conductivity, whereas the increase of the resistance in the Sm-\textit{CP} \textsubscript{A} phase can be explained by the submicrometer size isotropic droplets, which have larger resistance.

In summary, we have observed relatively fast and reversible light-induced photodarkening and bleaching in azo-containing antiferroelectric bent-core liquid crystals. The optical changes are accompanied by variations of the electrical properties such as the value of the spontaneous polarization
and electric field thresholds for switching between ferroelectric and antiferroelectric states. These observations imply interesting practical applications, for example optically addressed spatial light modulator (OASLM) devices. We note that similar optical switching of a calamitic antiferroelectric liquid crystal containing an azo linkage has already been studied and tested for OASLM applications [16]. The important difference between that and our present results is that in the calamitic antiferroelectric material the trans-cis isomerization required UV light whereas in the present case the effect works in the visible light range. Light-induced polarization decrease is also known in azo-dye-doped ferroelectric [17] and antiferroelectric [5,18] liquid crystals. However, because the dopant molecules disturb the ordering of the smectic liquid crystals, it is clear that molecules with incorporated azo linkages can represent advantages over the dopant systems.

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