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Photoinduction of optical anisotropy in an azobenzene-containing ionic self-assembly liquid-crystalline material

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Liquid-crystalline (LC) phase behavior and photoinduction of optical anisotropy in the ionic self-assembly complex 4-(4-diethylaminophenylazo) benzenesulfonate-dimethyldidodecylammonium (EO-C_{12}D) has been investigated by polarized light microscopy, differential scanning calorimetry (DSC), x-ray scattering, null-ellipsometry, and UV-visible absorbance techniques. The complex exists in a bilayer smectic-A (smA_2) LC phase at elevated temperatures (65–160 °C) and in a rectangular columnar (Col_r) LC phase in the temperature range of −5–65 °C. Hysteresis in the transition from the smectic to the columnar LC phase was observed. Detailed experimental investigations of the phase behavior, film-forming properties, and induction of optical anisotropy were performed. High values of photoinduced anisotropy (dichroic ratio of approximately 50) were detected when thin films of the complex were irradiated with linearly polarized light (Ar^+ laser, $\lambda = 488$ nm). It was shown that the azobenzene units align perpendicular to the polarization of the exciting light causing an alignment of the columns parallel to the light electric field vector. On the basis of all experimental results a model of the photoinduced alignment of the photochromic complex is proposed in which photoalignment of the material is connected to the reorientation of domains.

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I. INTRODUCTION

Generation of optical anisotropy upon irradiation with polarized light in certain photosensitive organic materials has been known since the beginning of the last century, i.e., the so-called Weigert effect [1]. This effect was studied in detail in viscous solutions containing azobenzene dyes [2] and in azobenzene dye-polymer blends [3]. The anisotropy induced in these systems is rather unstable. Stable photoinduced optical anisotropy was observed later in polymers containing chemically linked azobenzene chromophores [4]. Such photoinduced modifications in azobenzene-containing materials are very promising for optical data storage, optical processing, and photoalignment of liquid crystals [5–8]. However, studies of photoinduction of optical anisotropy were mainly focused on polymeric materials because of their good film-forming properties and stability of induced optical anisotropy in a glassy or liquid-crystalline (LC) state of the polymer.

Self-organized supramolecular materials, as a new class of materials, are currently a very active field of research [9–11]. Investigations are mostly focused on solving the structure and internal order in these materials and establishing structure-property-function relationships. Strategies employed to effect self-organization include H-bonding [12], metal-coordination [13], charge-assisted H-bonding [14], donor-acceptor type assemblies [15], and ionic self-assembly (ISA) [16]. A large number of these activities [17,18] is directed to generate mesophases where the mesogenic units are formed by intermolecular interactions. Manipulation of structural and macroscopic order in bulk solids and films, however, remains a major challenge for all of these approaches.

We have recently shown the existence of thermotropic liquid crystallinity in perylenebisimide-surfactant complexes based on the ISA strategy [19,20]. The properties of such complexes, produced by the facile combination of charged surfactants to oppositely charged building blocks (or tectons), can easily be tuned by careful choice of both moieties involved in the complex formation. In a proof-of-principle study (i.e., to show the potential for applications), different methods were tested to align one of the perylene-based LC complexes [20]. It was found that the materials' properties have a large influence on the processability, and therefore the alignment, of such materials. In order to understand the influence of the ionic interactions on the liquid-crystalline properties and alignment of the ISA complexes, detailed investigations of phase transitions, ordering, and alignment of the benzene-based ISA complex was performed [21]. However, from all our investigations and handling of ISA complexes we can conclude that alignment of ISA complexes is not a trivial task because each material requires an individual approach for its alignment.

Moreover, we have very recently shown that very effective alignment of the ISA complexes can be achieved when a photosensitive unit is incorporated directly into the chemical

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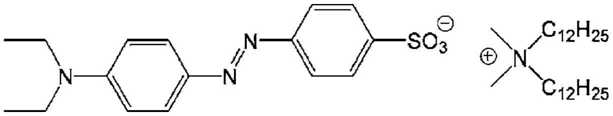

FIG. 1. Chemical structure of the EO-C_{12}D complex.

structure of the complex [22]. It was shown that the incorporation of azobenzene tectons into ISA complexes allow the photoinduction of very large dichroic ratios (DR=50) under irradiation with polarized light. In this paper we continue our investigations into the photogeneration of optical anisotropy in azobenzene-containing ISA complexes. In particular, we focus our attention on the photoinduction processes in the EO-C_{12}D ISA complex (see chemical structure of the complex in Fig. 1) for which the highest value of the anisotropy was obtained. The goal of this work is to understand the photoinduction processes in ISA complexes and their correlation to the phase structure of the complex. This goal was achieved by detailed experimental investigations of the correlation between phase behavior, film-forming properties, and photoinduction of optical anisotropy in the EO-C_{12}D complex.

II. EXPERIMENT

The EO-C_{12}D complex was prepared by 1:1 charge ratio mixing of two aqueous solutions (1 mg/ml) of EO (ethyl orange, Sigma-Aldrich) and C_{12}D (didodecyltrimethylammonium bromide, Sigma-Aldrich). The precipitated complex was then washed several times with deionized water to remove residual salt and then dried in vacuum. The structure of the complex is presented in Fig. 1. The resulting complex was then dissolved in chloroform or ethanol at an appropriate concentration (see next section) for further processing.

Polarized light photomicrographs were taken using a ZEISS Axioplane 2 microscope with strain-free objectives and a ZEISS AxioCam camera. The phase behavior of the complex was investigated by a differential scanning calorimeter (DSC). All DSC measurements were performed on a Netzsch DSC 200. The samples were examined at a scanning rate of 10 K min^{-1} by applying several heating and cooling cycles.

For the *in situ* temperature-dependent small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) experiments a Nonius generator (Cu $K\alpha$) was used, applying a position-sensitive detector (Inel). The samples were heated in an Anton Paar (Austria) heating chamber. The SAXS experiments in symmetric reflection were carried out on a Bruker D8 instrument with Cu $K\alpha$ radiation, using Goebel mirrors and a scintillation counter as a detector. In this setup the sample is fixed horizontally and the x-ray tube and detector moved.

Information about optical anisotropy in samples was obtained by performing transmission null-ellipsometry [23]. Using this technique one can estimate in-plane $(n_x-n_y)d$ and out-of-plane $(n_x-n_z)d$ retardation in the film. The thickness of investigated films was determined by measuring a scratch profile with AFM ("SMENA" Scanning Probe Microscope, NT-MDT, Russia).

The UV-visible spectra were measured with a Tidas UV-visible spectrometer (J&M). Temperature-dependent spectral measurements were performed by placing a sample, mounted on a THM 600 (Linkam) heating stage connected to a TMS 91 (Linkam) controller, in the beam. Temperature control of the samples was achieved within ±0.1 °C. The heating and cooling rate was 0.2 °C min^{-1}. Spectra were collected in the temperature range −40–150 °C in 5 °C steps. The peak wavelength of a spectral band was calculated as a wavelength which corresponds to the highest absorbance of the band.

Polarized visible spectra were measured with a Tidas UV-visible spectrometer (J&M) equipped with a Glan-Thompson polarizer, driven by a computer-controlled stepper motor (DC-500, Owis). The minimum and maximum absorbance yield a dichroic ratio $\text{DR}=A_{\max}/A_{\min}$.

Films were irradiated with a linearly polarized light of an Ar^+ laser ($\lambda=488$ nm). The intensity of the exciting light in the sample position was 50 mW cm^{-2}. The intensity of the exciting light was also varied in the range of 10–1000 mW cm^{-2} but the final results were qualitatively the same and dependent only on the exposure dose. Kinetics of absorbance and dichroic ratio changes under irradiation are presented as a function of exposure dose.

III. RESULTS AND DISCUSSION

A. Phase characterization

1. Polarized light microscopy

The EO-C_{12}D complex material shows a mosaic texture at room temperature under crossed polarizers when cast from a chloroform solution onto a glass slide [see Fig. 2(a)]. The mosaic texture is typical for highly ordered smectic phases [24,25] and indicates that the complex exists in a LC phase at room temperature. However, it is not possible to unambiguously identify the LC phase of the complex by only using polarized light microscopy. Only a cautious prediction can be made that the complex possesses a highly ordered layered structure.

2. Differential scanning calorimetry

The phase behavior of the complex was also investigated with differential scanning calorimetry (DSC). The DSC investigations showed several transition peaks [see Fig. 2(b)]. Peaks marked with **1** (−5 °C) correspond to a melting transition of crystalline alkyl surfactant tails, peaks marked with **2** (65 °C on heating, 15 °C on cooling) are connected to a "stretched-bent shape" transition of the surfactant alkyl tails. Similar transitions in these temperature ranges were also observed for pure surfactants and for other complexes containing the same surfactants [21]. These transitions are also accompanied by changes in the packing (aggregation) of the azobenzene (EO) units, as will be shown later. For the transition peaks **2** there is a clear hysteresis: on heating there are some structural changes connected with this transition, on cooling we observe supercooling and the same structural changes take place just before the onset of the crystallization of alkyl chains of the surfactant (peak **1**). The transition

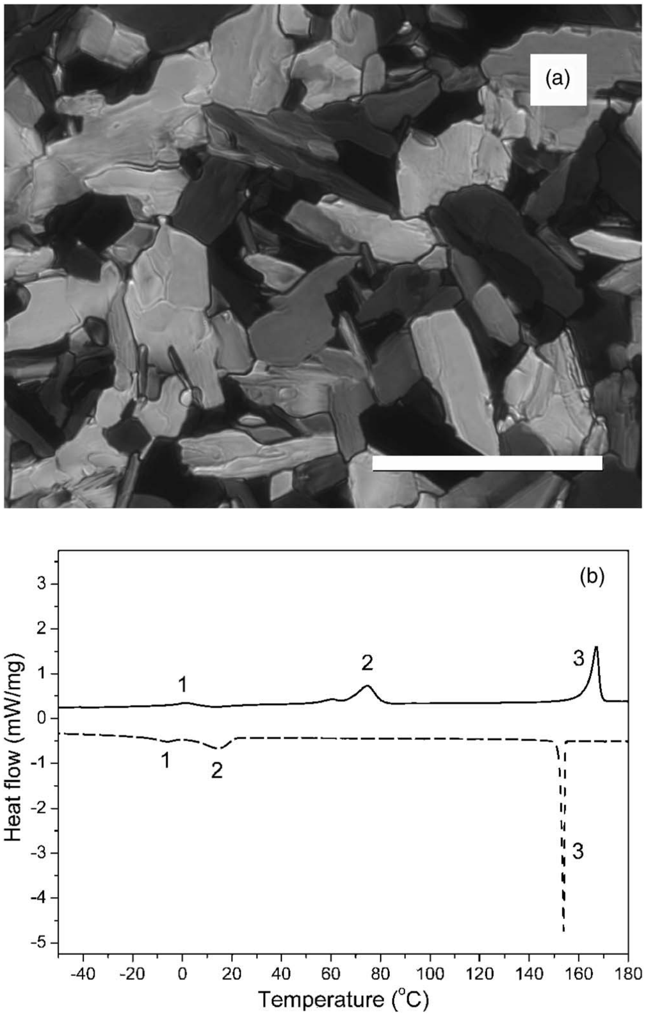

FIG. 2. (a) The mosaic texture of the EO-C_{12}D complex at 20 °C as observed in a polarized light microscope (crossed polarizers, bar: 25 μm). (b) DSC curves of the complex: (dashed curve) second cooling circle and (solid curve) second heating cycle.

peaks **3**, 165 °C on the heating curve and 155 °C on the cooling curve, respectively, are attributed to a change in the aggregation of the EO tectonic units effecting order in the complex (a shift of the maximum of π-π^* transition of the EO tectonic unit to the long wavelength region was observed above this transition, see below). It is noteworthy that this transition peak was not observed for the pure dye, indicating that this transition is specific for the formed complex. In addition, it should be noted that the complex was not heated above 180 °C during the investigations. This was done to prevent any degradation, as the degradation of the complex starts at 200 °C (as shown by TGA).

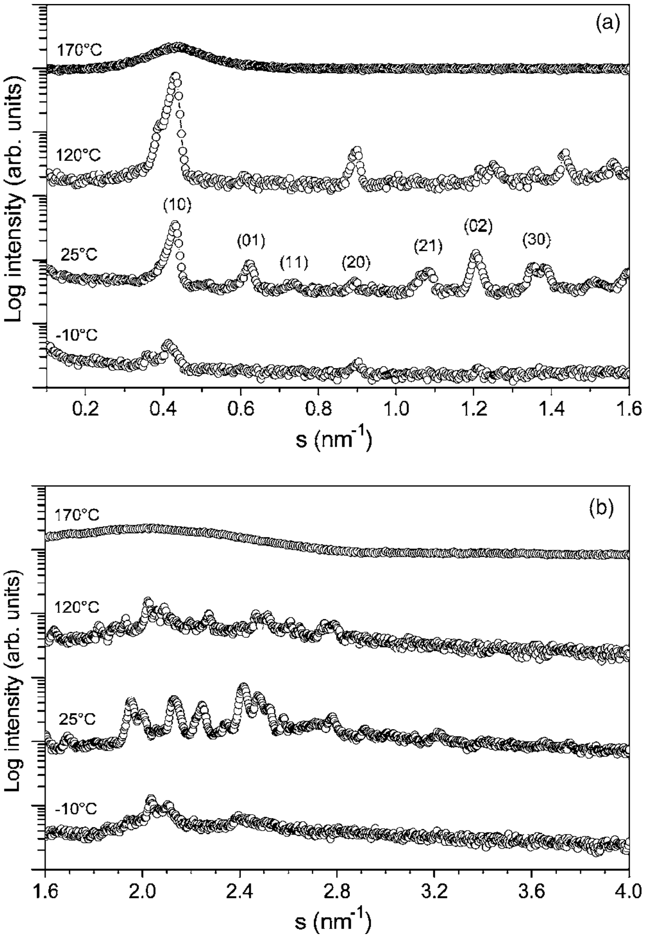

FIG. 3. (a) Small-angle and (b) wide-angle x-ray scattering diffractograms of the EO-C_{12}D complex recorded at −10, 25, 120, and 170 °C on heating.

3. Temperature-dependent x-ray investigations

In situ temperature-dependent x-ray scattering measurements were performed in order to identify the phases present in the material (Fig. 3). The data at $T=25$ °C show a sequence of well-defined reflections in the small-angle scattering region, which could be indexed as a two-dimensional (2D) rectangular phase with the dimensions a=1.64 nm and b=2.28 nm, i.e., a rectangular columnar ($\mathrm{Col_r}$) LC phase. The wide-angle x-ray scattering (WAXS) region indicates the presence of crystalline packing within the complex and is assigned to packing of highly aggregated azobenzene tectonic units. The intensity of these peaks is in correlation with the aggregation of the EO tectons: the highest aggregation is observed in the $\mathrm{Col_r}$ LC phase (see discussion below). At temperatures above ca. 65 °C the SAXS data significantly change into a series of equidistant peaks corresponding to repeat distance $d_0=2.25$ nm assigned to a lamellar bilayer LC phase (smectic-*A*, smA_2). From the WAXS data in this temperature range it is seen that aggregation behavior (packing) of azobenzene units is disturbed. The transition between columnar and smectic LC phases corresponds to transition peak **2** in the DSC curve. The transition between these LC phases is common for lyotropic phases of surfactants, however, such transitions have not been observed for thermotropic LCs. The reason for transition between columnar to layered phases is a change of phase volume of alkyl tails of the C_{12}D surfactant because of "stretched-bent shape" transition. Similar to DSC, the *in situ* x-ray scattering experiments reveal a significant hysteresis during the cooling process. The relaxation of the supercooled complex at room temperature from smectic to columnar phase is on the order of ca. 60 min

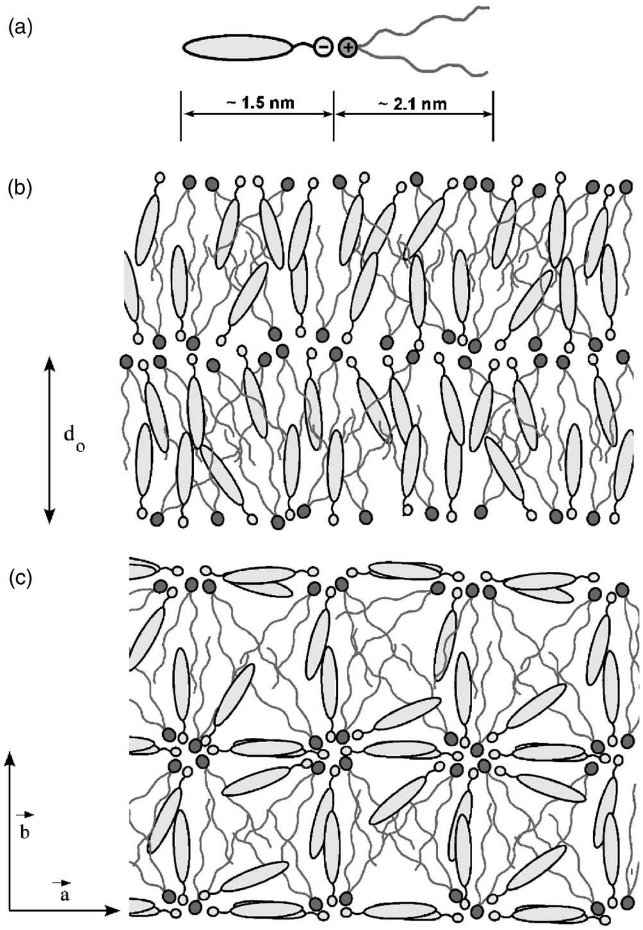

FIG. 4. Schematic representation of (a) molecular dimensions; (b) molecular packing of bilayer smectic-*A* (smA_2); and (c) molecular packing of rectangular columnar (Col_r) LC phases of the EO-C_{12}D complex.

and in accordance with other experiments (see below).

Heating of the complex above 165 °C leads to a change of the distinct SAXS pattern into a curve with a broad maximum centered at $s=0.4\ nm^{-1}$, in accordance to transition **3** observed in DSC. Evidently, this transition corresponds to the transformation of the regular phase into a weakly ordered morphology. It is assigned to a low-ordered LC phase, similar to that observed for other complexes [21]. X-ray data measured at −10 °C shows that the order in the complex below transition **1** in the DSC curve is strongly disturbed. It is connected to immobilization of alkyl tails into all-trans configuration which disturbs the columnar structure. This phase cannot be considered as a crystalline phase because of lack of the order, but rather classified as a glassy state. Taking into account the lengths of the surfactant C_{12}D and the EO unit (Fig. 4) reasonable models of molecular packing in columnar and smectic phases are suggested, in which side-length b (or layer repeat distance d_0) is commensurable with the C_{12}D unit and the shorter side *a* with the EO unit. The proposed molecular packing is also supported by the results of the characterization of photoalignment of the complex.

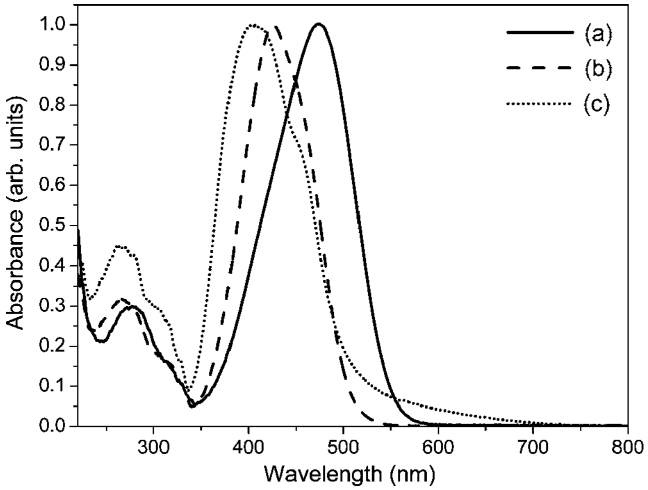

FIG. 5. Normalized UV-visible spectra of (a) ethyl orange in solution (water, $\sim 10^{-7}$ M); (b) EO-C_{12}D complex in solution (ethanol, $\sim 10^{-7}$ M); and (c) EO-C_{12}D complex in film.

B. Film-forming and aggregation properties

Comparison of the UV-visible spectra of pure ethyl orange dye in solution (water, $\sim 10^{-7}$ M), the complex in solution (ethanol, $\sim 10^{-7}$ M), and in thin film are presented in Fig. 5. The UV-visible spectrum of ethyl orange, of the EO-C_{12}D complex in solution and in film is characterized by the maxima at 475, 425, and 405 nm, respectively, which correspond to the strong π-π^* transition of the E isomer of the dye. The dramatic blueshift of the maximum of the azobenzene chromophores of the complex in ethanol, when compared with pure dye in water, might be a result of solvatochromic effect in solution or can be an indication of the existence of aggregates, even at such low concentrations because of a cooperative complex formation and aggregation process [16]. These two effects cannot be distinguished because we were not able to find the same solvent for both materials. However, there is a clear blueshift of the maximum in the spectra of the complex in films when compared with solution. These observations are typical for the parallel arrangement of chromophore dipoles forming H-aggregates [26]. The aggregation behavior is strongly influenced by packing considerations, phase transitions, and film preparation conditions. Therefore because aggregation processes strongly influence photochemical reactions in films, detailed investigations of the film-forming and aggregation properties of the complex were performed before starting investigations into the photoinduction of optical anisotropy.

The films of the complex were deposited by spin-coating (1000 rpm) on fused silica glass slides from chloroform solutions of the complex (5–100 mg/ml) at 25 °C. Films deposited from solutions with concentrations higher than 25 mg/ml showed pronounced scattering. The films deposited from the solutions of concentrations of 25 mg/ml and lower exhibited good optical quality. For all further investigations solutions of 25 mg/ml were used. The films deposited from this solution had thicknesses in the range of 100–200 nm. As determined with transmission null-ellipsometry and angular-dependent polarized UV-visible spectroscopy [21], the dipole transition moment of azobenzene dyes (EO) are oriented with a small preference in the plane of the film. The determined order parameter $S=-0.05\pm0.03$ results in a difference of the principal refractive indexes of $\Delta n=n_e-n_o=-0.05\pm0.03$ (at $\lambda=632.8$ nm). An increase of the thickness of the film, i.e., deposition from solutions of higher concentrations, leads to optically isotropic films at a thickness of about 1000 nm. Films with thicknesses less than 100 nm show a strong tendency for homeotropic orientation of the dipole transition moments of the azobenzene dyes, e.g., yielding a positive homeotropically oriented optical axis. This might be a result of influence of the interfaces. It is worth to note here that all experimental results present below are qualitatively the same for films of different thickness. From this reason the data for films deposited from the solution of concentration of 25 mg/ml are presented.

As aggregation processes are directly reflected in UV-visible spectra of the material, temperature dependent UV-visible spectral measurements on films of the complex were recorded. Changes of the spectra of the complex on heating-cooling of the material are shown in Fig. 6(a). The films of the complex were not heated above 150 °C because heating to the temperatures above the transition marked with **3** in Fig. 2(b) destroys the film by dewetting (but does not destroy the material). Changes in the spectra above 150 °C were measured in a thin layer of the complex between two fused silica slides. The absorbance of this thin layer was high because it was not possible to produce films of thickness less than a micrometer (presence of dust in the air during preparation). However, it was clearly detected that there is a strong and abrupt redshift of about 8 ± 2 nm of the absorbance maximum to the long wavelength region at elevated temperatures. This indicates that above the transition marked with **3** in Fig. 2(b) disruption of the aggregation of the azobenzene tectonic units takes place. From the spectra obtained in the consequent cooling and heating cycles, it can be seen that the azobenzene units are strongly aggregated in the rectangular columnar liquid-crystalline state [between peaks **1** and **2** in Fig. 2(b)]. The aggregation is enhanced if the film is left to relax at room temperature (see below). From Fig. 6(b) it is clearly seen that there is a hysteresis on the cooling and heating cycle. These changes correlate with the found hysteresis of peaks marked with a **2** on the DSC curves in Fig. 2(b).

Before providing an explanation of the temperature-dependent aggregation behavior, relaxation behavior in the spectra should be noted. After heating of the film to 150 °C (i.e., to the smA_2 LC phase) and subsequent cooling of the sample to 25 °C, relaxation of the complex to the aggregated state (the Col$_r$ LC phase) is observed (see Fig. 7, time-dependent measurement of the UV-visible spectrum at 25 °C). This relaxation is connected to the supercooling of the material, which was also observed by x-ray measurements (i.e., that on cooling from the smA_2 LC phase to room temperature the transition to Col$_r$ LC phase appears gradually). The complex stays in the smA_2 LC phase for at least 1 h at room temperature, and the transition to the Col$_r$ LC phase then appears gradually over several hours.

At elevated temperatures [above transition **3** in Fig. 2(b)] the complex exists in a low-ordered smectic-A (sm$A$) liquid-crystalline phase. In this phase, the azobenzene tectonic units practically do not aggregate, as indicated by the position of the absorbance maximum of the π-π^* transition near 425 nm, which is similar to that found for a diluted solution of the complex (see Fig. 5). On cooling below transition **3**, aggregation of the azobenzene units (EO) and the transition to an ordered smA_2 LC phase is observed. However, aggregation of the EO units in this phase is not as strong as might be expected, with the alkyl tails from the surfactant seemingly showing the largest influence on the structure formation (as supported by the fact that the interlayer distance correlates very well with the length of the surfactant, see Fig. 4). It is furthermore very interesting to note that stronger aggregation is observed at higher temperatures in this phase [see Fig. 6(b), temperature range 70–150 °C], indicating a slight demixing of the alkyl and azobenzene groups, up to the point where the phase transition to an overall lower-ordered LC state appears.

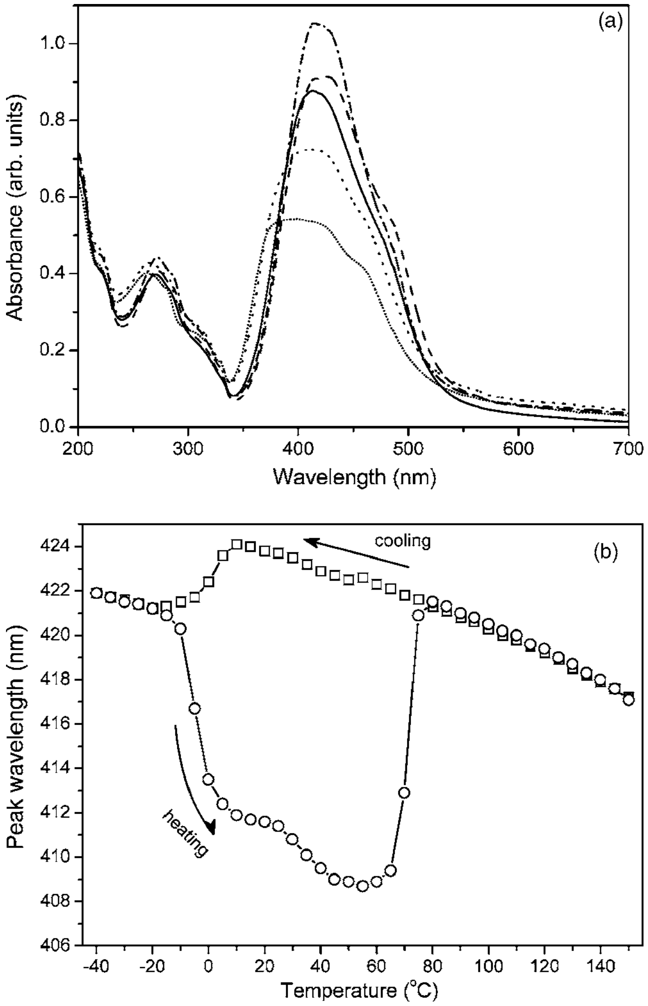

FIG. 6. (a) Changes of the spectra of the EO-C$_{12}$D complex on heating-cooling circle: (solid line) 150 °C; (dash line) 25 °C on cooling; (dash dot line) −20 °C; (dot line) 25 °C on heating; and (short dot line) 25 °C on the next day after relaxation. (b) Shift of the absorbance peak of the π-π^* transition of the EO tectonic unit in the complex on change of the temperature.

On further cooling to the temperature below the transition marked **2**, the alkyl tails straighten out and become less mo-

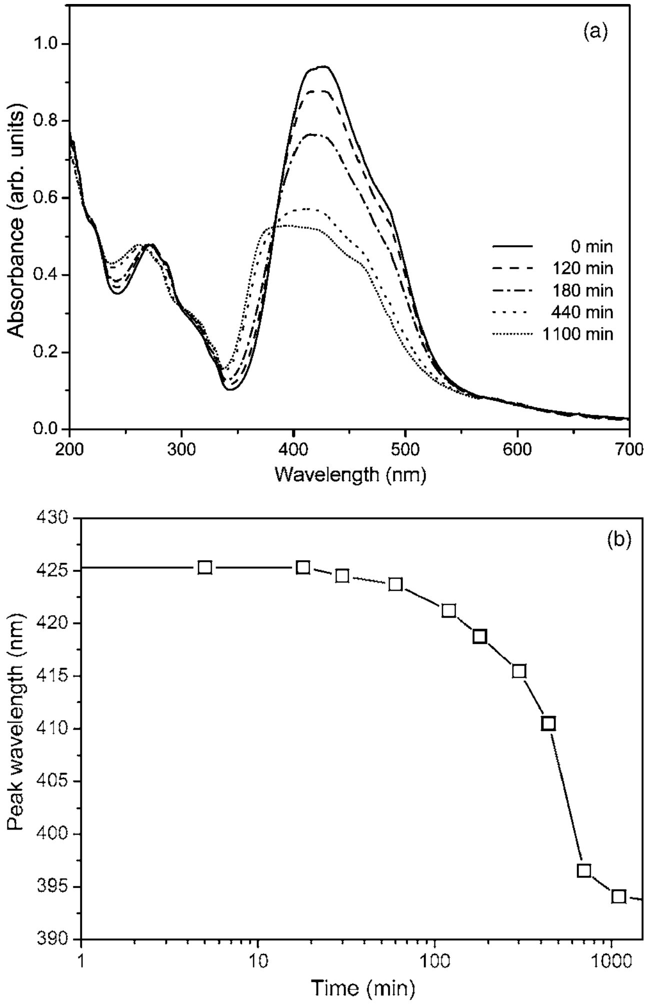

FIG. 7. Relaxation of the spectra of the EO-C_{12}D complex after heating to 150 °C and subsequent cooling to 25 °C; (a) relaxation of the UV-visible spectra and (b) shift of the peak wavelength on relaxation.

bile (a so-called alkyl rotator phase) [27]. The hysteresis will not be considered in this discussion and it is assumed that this transition appears around 65 °C. Because of this lowered mobility, the alkyl tails cannot fit between azobenzene units. It should be noted that in addition to this process, there is always phase separation of charged and noncharged fragments. Ionic interactions are much stronger than van der Waals and steric interactions, and to minimize energy within the material charges should form either layers, columns, or spheres, with noncharged fragments filling the free space between these structures. In our particular case x-ray measurements reveal that the transition to a columnar phase is found, which obviously provides the best way to accommodate the charged and noncharged fragments. One repeat distance is mostly the same as for the layered structure and corresponds to the surfactant length. The second repeat distance is in good agreement with calculated length of the EO tectonic unit (see Fig. 4). Conditions conducive to the aggregation of azobenzene units therefore exist in this phase. This type of behavior would also offer an explanation for the observed supercooling, already discussed. The formation of separate subphases, formation of separate charged layers, and the overall formation of a new phase requires a substantial amount of energy, and forces the formation of metastable states (that will only revert to the stable columnar phase over time).

Another way to induce the transition to the columnar phase is to cool the complex further to the crystallization temperature of the alkyl tails. In this case, the transition appears [see Figs. 2(b) and 6(b)], but the columnar phase is strongly disordered because of a lack of flexibility of the alkyl tails. On heating from the disordered columnar phase, there is melting of alkyl tails of the surfactant [transition marked with **1** in Fig. 2(b)]. The alkyl tails become flexible, and this allows better order in the system and the transition from a disordered (disturbed) columnar to a highly ordered $\mathrm{Col_r}$ LC phase. In this case, there is no restriction for the aggregation of EO tectonic units which is clearly reflected in the temperature-dependent spectral measurements on heating [see Fig. 6(b)]. On further heating to the bending temperature of the alkyl tails a transition to a highly ordered smA_2 LC phase can be observed. As was detected from temperature dependent x-ray measurements, the transition from smA_2 to $\mathrm{Col_r}$ and back is not complete. Some part of the material always exists in the smA_2 phase in the temperature range of the $\mathrm{Col_r}$ phase and vice versa. However, holding the complex for a long time (maximum 1 day) at 150 °C brings the complex to smA_2 phase and holding the complex at room temperature at least for 1 day brings the complex to the $\mathrm{Col_r}$ phase.

During the film preparation process of the complex, it was noticed that when solution of the complex was cooled to 20 °C or lower, films with very high optical quality were obtained. This was independent of the solution concentration and spin-coating conditions employed. After first annealing at 150 °C, these films show small light scattering. This metastable state of the film could appear because the surfactant alkyl tails are in all-trans configuration (crystalline in the film) state during the spin-coating process (additional cooling of the solution on evaporation of the solvent on spin-coating also has influence on this process). So, on deposition of the films, the tails in all-trans configuration restrict the aggregation of EO tectons that somehow influences optical properties of the films. As was determined experimentally the films in this state (prepared from cooled solution and not annealed) are temporarily stable and give reproducible results which are not dependent on film thickness and deposition conditions. Films deposited from solution at 25 °C or higher (and films prepared from cooled solution and annealed) also gave reproducible results, but they are quantitatively (but not qualitatively) dependent on the film thickness. So, for all further investigations films deposited from the cooled solutions without annealing were used.

C. Photoalignment properties

Having information about the phase behavior and film-forming properties of the EO-C_{12}D ISA complex, analysis of the induction of optical anisotropy in films of the complex could now be performed. It was very recently shown that

ISA complexes containing photochromic azobenzene moieties are capable of very effective induction of optical anisotropy [22]. In this paper we focus our attention on detailed experimental investigation and understanding of the processes which allow effective photogeneration of optical anisotropy. The EO-C_{12}D ISA complex showed the highest value of induced anisotropy (dichroism) in comparison to other complexes which have been investigated. This complex was therefore selected for further detailed investigations.

Thin films of the complex were prepared from cooled (15 °C) solutions by spin-coating. Neither UV-visible spectra nor optical texture exhibited any changes, even several weeks after film preparation. This means that film preparation from a cooled solution influences the optical properties of the films, but not the phase of the complex in the film. Comparison of optical textures of films prepared from cooled solution and the same films annealed at 150 °C for 1 h (or films prepared from heated solution) showed that the former films have very small domains and in latter ones domains are much larger in size [compare textures in the inset of Fig. 8(a)]. It was also noticed that thicker annealed films have larger domains. This therefore indicates that deposition from cooled solutions restricts only aggregation processes and the size of domains, but not the LC phase of the complex. Comparison of UV-visible spectra of annealed films of different thickness showed that thicker films are in a more aggregated state [compare spectra marked with **1** in Fig. 8(a)]. In addition, thick annealed films (with large domains) scatter light, which might also have an influence on the induction of optical anisotropy.

1. Influence of domain size

In order to investigate influence of domain size on the processes involved in the induction of optical anisotropy, two identical films (prepared under the same conditions with the same thicknesses) were prepared. One film was annealed at 150 °C for 1 h. Both films were irradiated with linearly polarized light of an Ar^+ laser of the same intensity. Changes of the spectra for both nonannealed and annealed films after irradiation with an exposure dose of 100 J cm^{-2} are shown in Fig. 8(a). Optical textures of these films before irradiation are shown in the inset of Fig. 8(a). The kinetics of the changes of the dichroic ratio versus exposure dose for both films are shown in Fig. 8(b). It is clearly seen that the efficiency of induction of the anisotropy is strongly dependent on domain size; the smaller the domain size, the higher the induced anisotropy. It should be noted that there is no saturation, even after an exposure dose of 100 J cm^{-2}. Very long irradiation and/or irradiation with higher intensity lead to steady increases of anisotropy. After very long and intense exposure (>1 kJ cm^{-2}), it is possible to reach a dichroic ratio of more than 35 for the annealed film as well. For nonannealed films, irradiation with an exposure dose of approximately 1 kJ cm^{-2} leads to a dichroic ratio of 50, with no saturation evident. A decrease of light scattering with increased exposure dose was observed. Since it was not clear how the size of domains influences the efficiency of induction of anisotropy, some additional experiments were performed to address this issue.

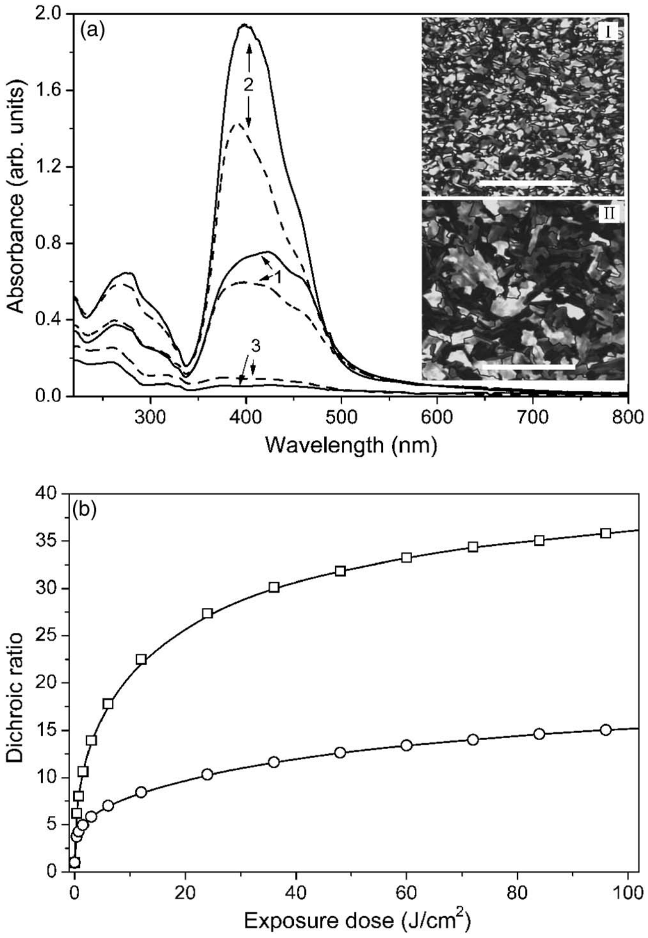

FIG. 8. (a) Changes of the polarized spectra of (solid line) nonannealed and (dashed line) annealed films of the EO-C_{12}D complex under irradiation with linearly polarized light of an Ar^+ laser ($\lambda = 488$ nm), (1) initial spectra, polarized spectra, (2) perpendicular, and (3) parallel to the polarization of the exciting light after irradiation with an exposure dose of 100 J cm^{-2}; Inset: optical texture of (I) nonannealed and (II) annealed films before irradiation (crossed polarizers, bar: 25 μm). (b) Kinetics of the changes of dichroic ratio calculated at 400 nm as a function of exposure dose for (□) nonannealed and (○) annealed film of the EO-C_{12}D complex.

Before looking for an explanation of the influence of domain size on the induction of anisotropy, a specific feature of the induction of anisotropy which was observed in all cases should be noted. If a film of the complex (annealed or nonannealed) is irradiated with small irradiation doses, a very pronounced jump in the anisotropy just at the beginning of the irradiation process (after an exposure dose of approximately 0.1 J cm^{-2}) is observed [Fig. 9(a)]. This anisotropy is temporarily stable after irradiation is stopped. Further irradiation leads to a very slow but gradual increase of the dichroic ratio. This behavior is very clearly seen from Fig. 9(b) and the inset. In this figure changes of spectra and kinetics of changes of absorbance at 400 nm under irradiation are shown. The biggest change of the dichroic ratio of 7 for nonannealed films with a very small domain size was observed at the beginning of the irradiation. The smallest change of dichroic ratio of 2 was observed for annealed films

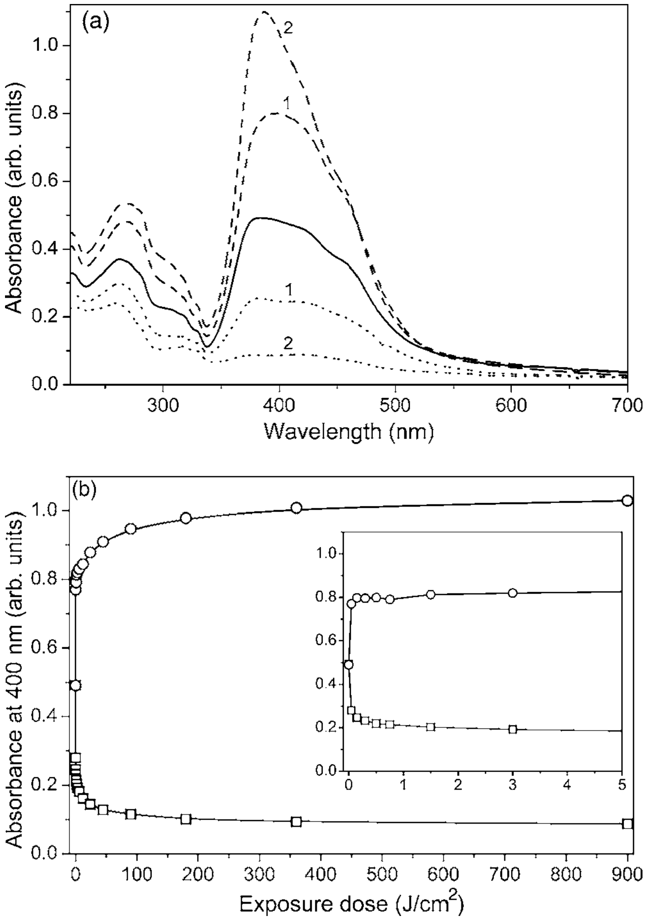

FIG. 9. (a) Changes of the polarized spectra of annealed film of the EO-C_{12}D complex under irradiation with linearly polarized light of an Ar^+ laser ($\lambda=488$ nm): (solid line) initial spectrum and spectra (dotted line) parallel and (dashed line) perpendicular to the polarization of the exciting light after exposure dose of (1) 0.15 J cm^{-2} and (2) 900 J cm^{-2}. (b) Kinetics of the changes of absorbance at 400 nm of annealed film of the EO-C_{12}D complex (□) parallel and (○) perpendicular to the polarization of the exciting light as a function of exposure dose.

with very large domains. From this experiment, the conclusion can also be drawn that the domain size has a direct influence on the processes of induction of optical anisotropy.

2. Changes during the photoorientation process

In order to follow the changes within domains on irradiation, the following experiment was carried out. A film of the complex is annealed in order to get domains large enough to observe and clearly distinguish in a polarized light microscope. In order to ensure that the same area was investigated at later stages, marks (scratches) were made on the film. The film was then irradiated with small irradiation steps and images of the same area were recorded in the polarized light microscope. The results of this investigation are presented in Fig. 10. The following observations can be made: from comparison of the pictures at small irradiation doses reorientation of small domains and enlargement of large domains is observed. On further irradiation, a division of large domains into smaller parts is observed. From this experiment, the conclusion can be made that reorientation of the azobenzene (EO) units is not local, like in polymers, but a cooperative process which leads to the reorientation of domains. Small domains reorient under irradiation to align the dipole moments of the photosensitive units perpendicular to the polarization direction of the exciting light. Very large domains cannot undergo such reorientation, and they simply divide into smaller parts. Finally, the domains which are already aligned combine, which leads to an increase of the size of these domains. Finally, all domains align in such a way that all azobenzene units become mostly perpendicularly aligned to the exciting light polarization. This means that columns of charges (and stacks of azobenzene units between these columns) in the complex align parallel to the polarization of the exciting light. The smaller the size of the domains, the more effective the photoreorientation process. The first big increase in the anisotropy (Fig. 9) is therefore caused by the reorientation of domains of small size. Further reorientation of domains of large size needs larger exposure doses for their division and further reorientation, which would explain the last, slower part of the orientation process, as can be seen from Fig. 9(b).

Observation of domain reorientation under irradiation with polarized light does not give information about the real molecular process within domains when they reorient. These processes could include (a) mechanical rotation of domains under irradiation with polarized light or (b) transition of domains into a highly disordered state under irradiation, followed by a transition back to a highly ordered state where the probability of domain excitation is lower (i.e., the case where azobenzene units are perpendicular to the light polarization). The possible process of domain reorientation by transition within domains in some kind of disordered state can be excluded because of the following reasons. First of all, it is worthy to note that (i) no transition to the isotropic state of the complex is observed before degradation of the material; (ii) films of the complex can be destroyed by dewetting on heating to the low ordered sm*A* phase; and (iii) the photoalignment kinetics were not dependent on the light intensity. Even at very high light intensities the films were not destroyed because of the possible transition to a low ordered sm*A* phase (local heating under light absorbance). No change in absorbance spectrum (redshift of the absorbance maximum) related with the break of aggregation of azobenzene units, which was caused by the transition to the highly ordered sm*A* phase, was observed under irradiation in with different intensities. All these factors indicate that the complex in the film under irradiation remains in a columnar phase. The reason for the stability of columnar phase under irradiation is connected to the properties of the complexes. Recently, it was shown that ionic interactions hold the complex in an ordered state, even if all fragments should be in an isotropic phase [21]. To reorient the domain all columns should therefore be reoriented together. It means that the only way to reorient the system is to mechanically rotate the whole domain. From all this discussion of and comparison of results it is possible to conclude that reorientation of the domains is connected to their mechanical rotation and this is a cooperative process. Small domains need small torque to

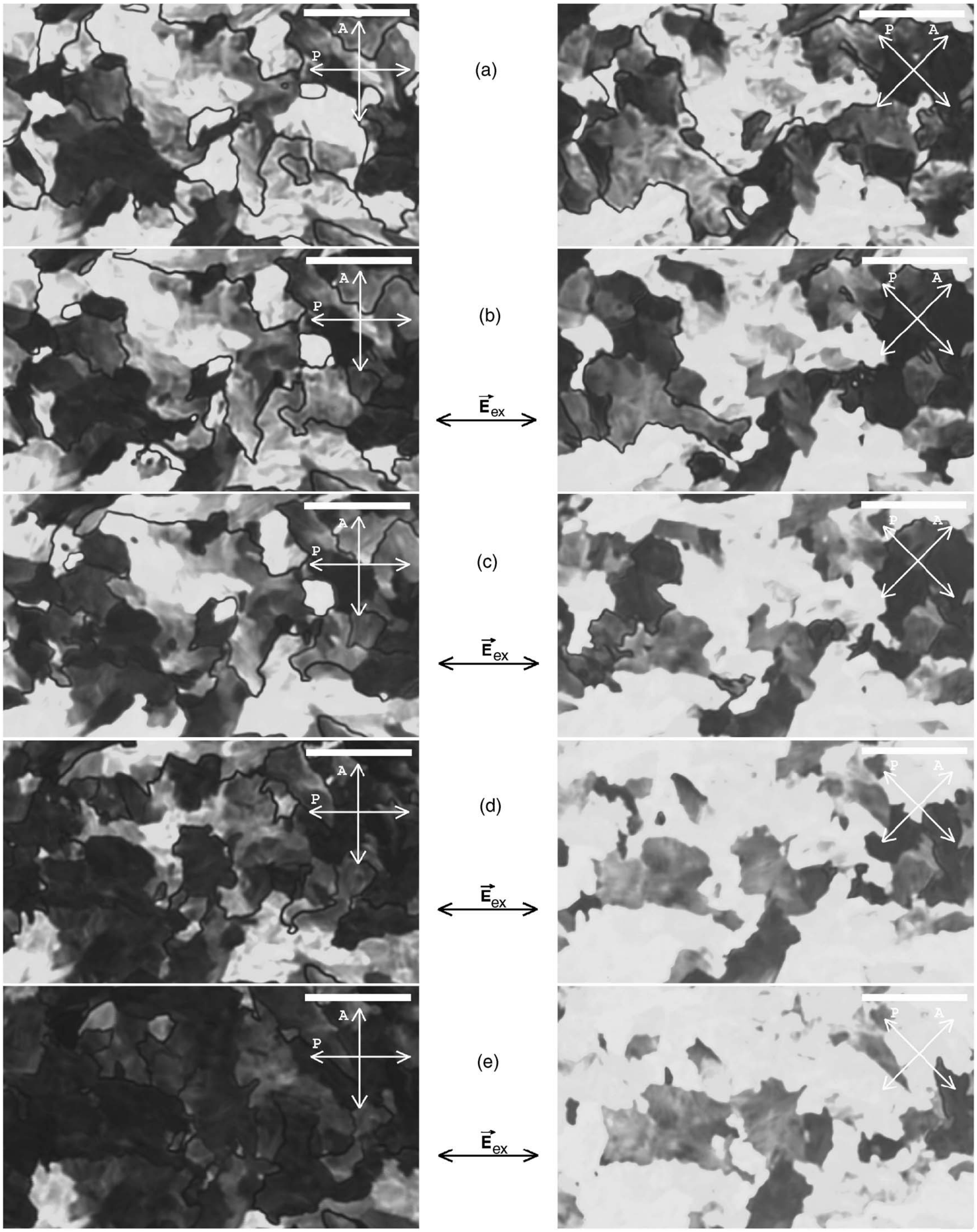

FIG. 10. Changes of optical textures in the same area of annealed film of the EO-C_{12}D complex under irradiation with linearly polarized light of an Ar^+ laser ($\lambda = 488$ nm): (a) initial texture, and textures after exposure dose of (b) 0.15 J cm^{-2}; (c) 3 J cm^{-2}; (d) 90 J cm^{-2}; and (e) 900 J cm^{-2} (crossed polarizers, bar: 10 μm). P and A indicate directions of transmission axes of polarizer and analyzer, E_{ex} indicates the polarization direction of the exciting light.

their reorientation. For bigger domains the threshold is too high to prepare such rotation, and they simply divide into smaller ones and then rotate.

Reorientation (rotation) of domains as a whole is a cooperative process. Cooperativity in general is connected to behavior of a system as a whole and usually characterized by threshold (critical concentration, external field, force, momentum, energy, and others). Pure cooperative processes would be, for example, Friedericksz transition in a liquid crystal cell (critical field). The threshold for domain reorientation is a critical torque (created by pumping of the domain with light) needed to rotate the domain. The presence of this critical torque was observed in all kinetics: for films prepared in the same conditions the initial jump in the anisotropy [see inset in Fig. 9(b)] was dependent on light intensity. From comparison of kinetics of dichroic ratio versus exposure dose for different light intensity it was noticed that the higher the light intensity was, the bigger the first jump of anisotropy was. If one is to assume some kind of domain size distribution (starting practically from zero, having a maximum, and ending with maximum domain size) then the higher intensity will cause more domains to reorient under initial light pulse. This is a clear indication of threshold existence and cooperativity of the photoalignment of the complex. The origin of this cooperativity can be therefore found in the induced order in the LC phases owing to the presence of the ionic interactions in the complex.

This type of behavior is in contrast to polymers in the glassy state where the photoalignment is a local process. However, in the literature the term "cooperativity" is usually used instead of correlation and even instead of phase transition. In photosensitive polymers, temporal stability of the photoalignment can be realized if the photosensitive units are attached to a polymer matrix. There is a correlation between matrix and photosensitive units. This correlation extends to several molecular dimensions, the correlation length. The alignment processes in this case are clearly local (one might say locally cooperative but it stays local) and happen in a glassy state of the polymer (practically all investigated polymers are in a glassy state). If, for example, the correlation length within a LC domain is bigger than domain size, then the reorientation processes will be cooperative within the domain. Cooperativity in photosensitive polymers might be observed if one takes an aligned LC polymer in a LC state and tries to reorient it. A threshold in intensity should exist, but it is not clear if above this threshold the system will reorient as a whole, or if there is a simple transition to the isotropic state under photochemical reaction and back transition to the aligned LC state. A further example where the term cooperativity is also used can be found: If a polymer is irradiated in the glassy state to introduce a low degree of anisotropy and then heated to the LC state, there is an amplification of order after annealing in the LC state. However, this process is simply a phase transition with centers for transition. A similar process appears if a LC is cooled from the isotropic phase to a LC phase in a cell with aligning layers (in this case the centers are at the interface with aligning layers).

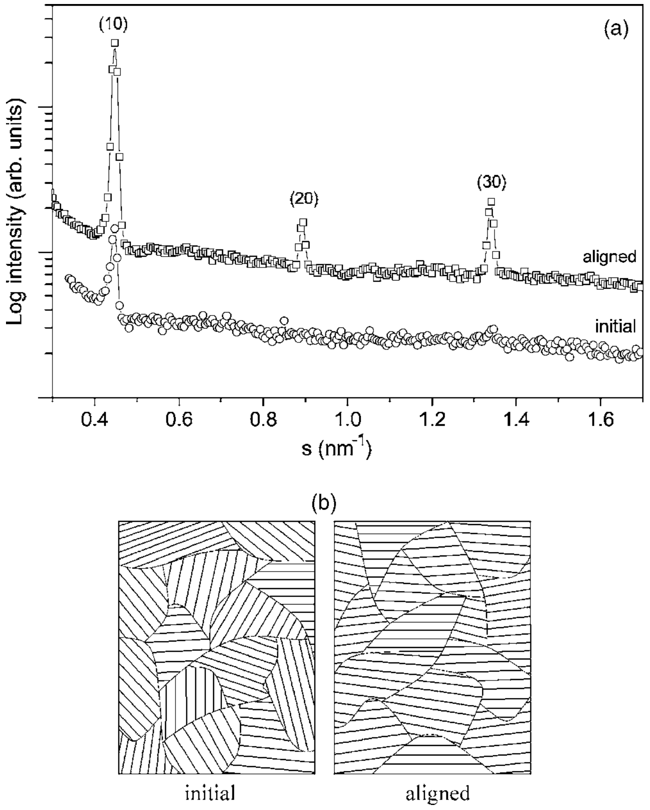

FIG. 11. (a) Small-angle x-ray reflectivity measured on an initial and aligned film sample of the complex at room temperature. (b) Schematic representation of order of columns within domains for an initial and aligned sample.

3. Changes after irradiation

Irradiation of films of the EO-C_{12}D complex leads to alignment of columns parallel to the polarization of the exciting light whereas the long axes of the photosensitive azobenzene units are perpendicular to the columns. These columns are parallel to the substrate because the electric field vector of the exciting light is parallel to the substrate. The liquid-crystalline phase of the complex is columnar rectangular with dimensions of 2.28 and 1.64 nm. In order to elucidate the orientation of the rectangular structure relative to the substrate, SAXS measurements were performed on samples before and after irradiation [Fig. 11(a)]. While the irradiated (aligned) sample shows a sequence of equidistant (h0) reflections with $d=2.28$ nm, the nonirradiated (initial) one only shows the first interference maximum. First, these results prove that indeed the columns are parallel to the substrate in both cases. Second, the damping of the higher order reflections for the nonirradiated material suggests that the liquid-crystalline domains are isotropically distributed in the plane of the film. Irradiation leads to an alignment and consequently to an enforcement of the (h0) peaks [see Fig. 11(b)]. In both cases planes of columns which correspond to repeat distance b [Fig. 4(c)] are parallel to the substrate.

A specific effect connected to molecular order in the complex that has never been observed in photosensitive polymers should also be noted. If one looks at the changes in the UV-visible spectra after irradiation [Figs. 8(a) and Fig. 9(a)], it is seen that in addition to the alignment of the dipole moments of the azobenzene photosensitive units, alignment of the dipole moments of the benzene rings which are part of the EO photosensitive unit (peak of absorbance around 270 nm, π-π^* transition) is also observed. The dipole transition moment of this transition is parallel to the plane of the benzene ring. In azobenzene-containing polymers, for example, benzene rings are isotropically distributed, even in the aligned state. In the case of the EO-C_{12}D ISA complex, planes of benzene rings are aligned perpendicular to the polarization direction of the exciting light.

From all the information obtained about the order and the photoalignment of the complex, one can conclude that the complex aligns under irradiation with polarized light with columns parallel to the polarization of the light. Azobenzene

(EO) tectonic units are perpendicular to the columns. Azobenzene units are aggregated in stacks between columns of charges in a way that planes of benzene rings are perpendicular to the stacks.

Finally, an answer to the question about distribution of azobenzene units around columns of charges should be given. From x-ray data, it is proposed that in the smA_2 LC phase of the complex azobenzene units of the EO tectons are mixed in a layer with alkyl tails of the surfactant. In the $\mathrm{Col_r}$ LC phase the azobenzene units are separated and form aggregated stacks between columns. However, it is not clear if distribution of azobenzene units around columns of charges is really isotropic. The following results should shed some light on this question. In the case of an isotropic distribution of azobenzene units around columns and unidirectional alignment of the columns in the plane of the film, the absorbance in the plane perpendicular to the columns will be the same in all directions. However, in the case of an anisotropic distribution, this effect will not be easy to measure by polarized tilted UV-visible spectroscopy [21] because the anisotropic distribution of the refractive index has a strong impact on beam propagation on tilting the sample. In this case measurements of spatial refractive index distribution far from the absorbance band of the azobenzene units will be the best choice to answer the question about distribution of azobenzene units because there is direct correlation of refraction index dispersion with absorbance. For this purpose, a nonannealed film prepared from cooled solution was irradiated with an exposure dose of about 1 kJ $\mathrm{cm^{-2}}$ in order to get maximum alignment in the film. This film was characterized with null-ellipsometry supplemented with thickness measurements. Modeling of the experimental curves gives the following results: $n_x - n_y = 0.30 \pm 0.02$, $n_x - n_z = 0.10 \pm 0.02$, $n_z - n_y = 0.20 \pm 0.02$, and $n_z - (n_x + n_y)/2 = -0.05 \pm 0.02$, where xy – is the plane of the film and y is parallel to polarization direction of the exciting light. In this configuration xz – is the plane of distribution of the azobenzene units. This experiment clearly shows that $n_x > n_z > n_y$ and azobenzene units are preferably distributed in the plane of the film, i.e., in the $\mathrm{Col_r}$ LC phase they are separated from layers (which are parallel to the substrate) to form stacks between columns. This is in perfect agreement with the proposed model of molecular order in the complex. It should be noted that the out-of-plane anisotropy was not changed under irradiation process: $n_e - n_o$ (before irradiation) $= n_z - (n_x + n_y)/2$ (after irradiation) $= -0.05 \pm 0.02$. This, in addition, supplements the previous conclusion that under irradiation columns reorient in the plane of the film, and there are no changes in the out-of-plane direction.

IV. CONCLUSIONS

The phase behavior and photoalignment of the EO $-\mathrm{C_{12}D}$ ISA complex have been investigated in detail. Above 160 °C, the complex exists in a low-ordered LC phase. On cooling the complex exhibits a transition to a highly ordered bilayer smectic-A (smA_2) LC phase and then to a highly ordered rectangular columnar ($\mathrm{Col_r}$) LC phase near 65 °C. Below −5 °C, the order in the complex is disturbed due to immobilization of alkyl tails of the surfactant into all-trans configuration, which causes a transition to a glassy state. The transition from smA_2 to $\mathrm{Col_r}$ LC phase shows a marked hysteresis on cooling: supercooling was observed and this transition appears almost simultaneously with the onset of crystallization of the surfactant tails. The transitions from the smA_2 to $\mathrm{Col_r}$ and back are caused by the change of phase volume of alkyl tails of the surfactant on their “stretched-bent shape” transition.

Optical properties of films of the complex depend on preparation conditions and thermal treatment. Films deposited from cooled (20 °C and lower) chloroform solution exhibit very good optical quality while films deposited from chloroform solutions at 25 °C or higher (or films annealed at 150 °C) scatter light. Light scattering is connected to size of domains. In the case of films deposited from cooled solution, the formation of large domains is restricted.

We observed an effective photoalignment of the complex under irradiation with polarized light. A dichroic ratio of 50 has been obtained. The photoalignment of the complex depends strongly on the size of the domains. In the case of small domains, the photoalignment is the most effective. Photoreorientation in the complex is not local like in azobenzene-containing polymers, but is a cooperative process and connected to the reorientation of domains. Domains in the initial film are aligned in such a way that columns of the complex are parallel to the substrate with isotropic orientational distribution parallel to the film plane. During irradiation, there is an in-plane reorientation of domains (columns). Photoalignment in the photosensitive ISA complexes strongly depends on internal order in the complex. Our study reveals that the investigation of correlation between molecular packing, chemical structure, and photoalignment in the ISA complexes is very important to understand these processes and their applications.

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