Photoinduced Self-Organization and Photoorientation of a LC Main-Chain Polyester Containing Azobenzene Moieties

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ABSTRACT: Light-induced ordering processes were investigated in spin-coated films of a smectic main-chain polyester with mesogenic 4,4′-dioxyazobenzene groups in the backbone. Spin-coating results in aggregation due to $\pi-\pi$ stacking and out-of-plane orientation. Both are destroyed by UV exposure. However, they are rebuilt by subsequent thermal *Z*/*E* isomerization of the azobenzene groups, forming a lamellar structure parallel to the substrate. The irradiation with linearly polarized visible light results in the orientation of the azobenzene moieties perpendicular to the electric field vector, preserving the lamellar structure with values of dichroism up to 0.43. However, the efficiencies of the *E*/*Z* photoisomerization and that of the photoorientation process strongly depend on the history of the sample. The scanning force microscopy (SFM) histogram indicates two types of domains in the top layer, one oriented in the normal and the second one formed by tilted azobenzene groups with an average tilt angle of about 50° to the normal. The last spacing is erased by annealing, but is rebuilt due to linearly polarized exposure. The photoinduced anisotropy of a “wet” dewetted ultrathin film of 5 nm is 1 order of magnitude smaller. It demonstrates that the photoreaction and the self-organization influence each other mutually.

I. Introduction

Films of functionalized polymers with liquid crystalline, light-sensitive, or specific optical properties are of great importance for optical technologies.[1] Polymers with photochromic azobenzene moieties are very promising materials for reversible optical data storage,[2−6] optical processing,[7] as “command layers” for the alignment of liquid crystals,[8,9] or the photochemically driven formation of surface relief gratings.[10−13] Resulting anisotropic optical components such as retarders, polarizers, or holographic gratings have a strong impact on optical technologies.[14] However, the creation of anisotropy in organic materials is of general interest in material science to improve physical properties of devices due to an anisotropic morphology. All applications as passive or active elements require the preparation of stable films, the establishment of precisely controlled 3D order and, in many cases, photopatterning. While a high stability of the order is a necessary condition for passive optical elements, reversible changes of the order and related optical properties are required for switchable elements.

Recently, it was shown that thin films of liquid crystalline side-chain polymers[15,16] undergo a spontaneous self-organization process upon preparation and annealing of spin-coated films, forming macroscopically ordered monodomain films in which the smectic layers are arranged parallel to the substrate.[17−20] Thus, the mesogenic side groups become homeotropically aligned. More recently, it was shown that smectic main-chain polyesters containing rodlike aromatic mesogenic moieties and a flexible alkyl spacer in the backbone undergo a comparable spontaneous self-organization process[20] upon annealing in the mesophase. Contrary to the usual behavior of smectic main-chain polymers, the backbone of this polymer does not adopt a nearly stretched conformation.[19] The intrinsic molecular mobility of the polymer backbone was enhanced by annealing at temperatures of the S_A phase. The relaxation of the polymer led toward a lamellar equilibrium state, in which the azobenzene units are homeotropically aligned and aggregated in one part, whereas the phenyl malonate and alkyl spacers forming numerous hairpins are segregated in layers between.[19] However, spin-coated films thinner than 7 nm exhibit a completely different ordering behavior. These films undergo a “wet” dewetting process forming holes and rims, whereas in the holes, planar aligned monolayers are anchored to the substrate.[20]

The photoisomerization of azobenzenes establishes a wavelength-dependent steady state between rodlike *E* isomer and banana-like *Z* isomer. In addition to absorbance, the molecular shape, polarity, and the direction of the transition moment are changed. This results in the light-induced temporary variation of the intermolecular interactions decreasing the LC order and the aggregation in ordered films.[21−23] Moreover, the *E*/*Z* photoisomerization results in a higher molecular mobility, decreasing the glass transition temperature (T_g) and the phase transition temperatures.

Irradiation of azobenzene-containing polymers with linearly polarized (LP) light can result in the orientation of the azobenzene moieties perpendicular to the electric field vector of the incident light.[2−5,24,25] This photoinduced orientation process occurs in the steady state of the *E*/*Z* photoisomerization, even within the glassy state of amorphous and LC side-chain polymers.[24−27] It takes place via repeated angular-selective excitation events, a number of *E*/*Z* photoisomerization cycles, and rotational diffusion in the steady state of the photoreaction minimizing further excitation.[28] The photoorientation process provides orientation in initially isotropic films

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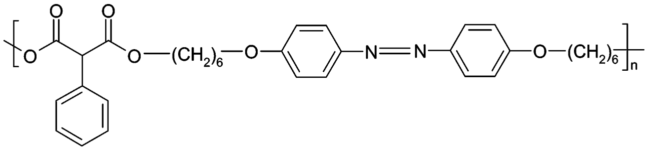


Figure 1. Chemical structure of the polymer.

of amorphous[26] and liquid crystalline side-chain polymers[27] and the reorientation in aligned films of LC polymers[28,29] or LB multilayers[23,30] as well. Surprisingly, photoinduced birefringence can be achieved at comparable levels and with comparable rates, even when the chromophore is tightly bound within the main-chain of polymers.[31−33] In the case of LC polymers, the interaction between the ordering impact of the linearly polarized light and the thermotropic self-organization results via much more complex behavior. Therefore, in aligned films, the photoreorientation can be restricted by the initial order.[29,34] On the other hand, in the case of LC polymers, the photoinduced order can be significantly amplified by annealing in the mesophase. A small value of photogenerated anisotropy induced in the glassy state can act as an aligning force for the thermotropic self-organization process.[35,36] Therefore, both ordering principles can interact in a competitive or constructive way. Very recently, it was reported that photoorientation and its amplification is strongly influenced by the initial order of the films.[37,38]

The aim of the present investigation is to study light-induced ordering processes of an azobenzene-containing liquid crystalline main-chain polymer upon irradiation with UV light or, alternatively, with linearly polarized visible light.

II. Experimental Section

LC Polymer. A liquid crystalline main-chain polyester with photochromic azobenzene groups was used as model for the investigation. The repeat unit of the backbone contains a phenyl malonate group and a rodlike (*E*)-4,4′-dioxyazobenzene group as a mesogenic moiety, which are connected by two hexamethylene spacers (Figure 1).

The synthesis[39] and ordering in thin films[19,20] is described elsewhere. The molecular weight is 8.56×10^3 g/mol and was obtained from the peak maximum from the GPC elution diagram.[19] Differential scanning calorimetry (DSC), polarization microscopy, and X-ray diffraction reveal a glass transition temperature at 29 °C, a S_B phase between 29 and 54 °C, and a S_A phase between 54 °C and the clearing temperature at 117 °C. The thickness of the smectic layers of about 3.5 ± 0.1 nm was determined by X-ray diffraction.[19] The polymer chains do not adopt a rather completely predominantly stretched conformation in the smectic phase. They are almost regularly folded, forming hairpins.[19]

Film Preparation. Thin films of the polymer were prepared by spin-coating on silica glass substrates or, alternatively, on silicon wafers (Aurel, Germany). The polymer was dissolved in a 50:50 (v/v) solvent mixture of dichloroethane and chloroform or, alternatively, in tetrahydroforan (THF). Each substrate was covered completely with the polymer solution and rotated at 2000 rps for 30 s. A 10 mg/mL polymer solution leads to a film thickness between 10 and 15 nm. Increasing concentration results in thicker films. The annealing procedure of the films was carried out in air by using a hot plate.

SFM Measurements. SFM measurements were performed with a Nanoscope IIIa (Digital Instrument Inc., Santa Barbara, CA). Image acquisition was done at the air−polymer interface in the Tapping Mode at room temperature (25 °C). In this mode, the cantilever is oscillating vertically at its resonance frequency touching the sample surface per period. Therefore, lateral shear forces (and accordingly also tip-induced sample degradation) are minimized. Silicon cantilevers (length 125 μm, width 30 μm, thickness 3−5 μm) with a spring constant between 17 and 64 N/m and a resonance frequency in the range of 240−400 kHz were used. The interaction with the sample causes also a phase shift of the oscillation, which is related to the viscoelastic properties, i.e., also to the hardness of the sample.[40]

UV−Vis Spectroscopy. A Lambda 2 spectrometer (Perkin-Elmer) was used to measure the UV−vis absorbance. The angular dependence of absorbance was detected by using a photodiode array UV−vis spectrometer (Polytech, XDAP V2.3) in combination with a computer-controlled Glan−Thomson prism. By rotating the polarizer, the spectra were measured at each 5° to find the maximum and minimum of the orientational distribution. The dichroism $d = (\mathrm{abs}_{\max} - \mathrm{abs}_{\min})/(\mathrm{abs}_{\max} + \mathrm{abs}_{\min})$ was calculated at the wavelength of the maximum of the $\pi-\pi^*$ absorbance. The out-of-plane order parameter, $S_h = 1 - F$, was derived from the average absorbance of the initial sample ($\mathrm{abs}_{\mathrm{initial}}$) or of the isotropic melt and the average absorbance of the homeotropically aligned film ($\mathrm{abs}_{\mathrm{aligned}}$) with $F = \mathrm{abs}_{\mathrm{aligned}}/\mathrm{abs}_{\mathrm{initial}}$. Temperature-dependent measurements were carried out by using a home-built heating stage with a temperature controller (EROTHERM 920 P).

The $\pi-\pi^*$ transition of the (*E*)-azobenzene moiety is directed along the long molecular axis, whereas the $\phi-\phi^*$ transition of the aromatic rings does not exhibit any polarization dependence.[20] Therefore, it can be used as an internal standard to normalize the $\pi-\pi^*$ absorbance. The ratio of both absorbances characterizes the out-of-plane orientation of the azobenzene moieties.[20]

Irradiation. The UV irradiation (365 nm, 7 mW cm^{-2}) was carried out in a setup consisting of a HBO lamp (100 W Osram), a metal interference filter, and a water-filled cuvette suppressing the IR irradiation. The linearly polarized visible irradiation to generate the photoorientation was carried out by using an Ar^+ laser (Coherent, Innova 90−4) at 458 nm and a power density of 50 mW cm^{-2}. The experiments in THF solution were carried out at a concentration of 10^{-5} mol/L with respect to the repeat unit.

III. Results and Discussion

Photochemical Modification Due to UV Light. The UV−vis absorption spectra of the polymer dominated by the (*E*)-4,4′-dioxyazobenzene chromophore is displayed in Figure 2.

Upon UV irradiation (365 nm) of the polymer in THF, the strong $\pi-\pi^*$ absorbance of the azobenzene group decreases, while the absorbance of the $n-\pi^*$ transition is increased, due to the *E*/*Z* photoisomerization. The $\phi-\phi^*$ transition of all aromatic groups at 250 nm does not show any significant variation. The kinetics of the photoisomerization and the thermal *Z*/*E* isomerization in solution cause isosbestic points at 321 and 431 nm. A steady state is established upon irradiation with 365 nm, characterized by a proportion of about 0.95 of the *Z* isomer, while the irradiation with visible light of 458

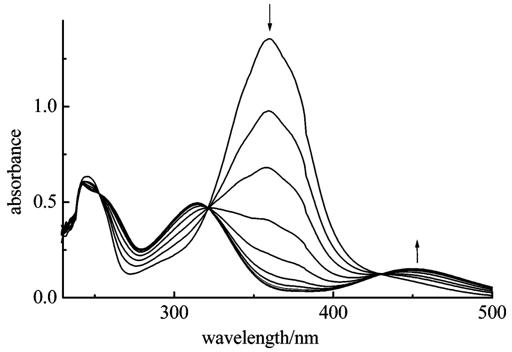


Figure 2. Change of absorbance of the polymer in THF solution during irradiation ($\lambda_{ex} = 365$ nm, at 0, 1, 2, 3, 4, 5, 6, 8, 15, and 30 s, $P = 7$ mW cm^{-2}).

nm establishes an *E* isomer, reaching dynamic equilibrium. In the dark, the *E* isomers are rebuilt by thermal *Z*/*E* isomerization. The behavior of the photochromic main-chain polymer in solution is identical with that of the related monomeric azobenzene derivative.

Figure 3 shows the spectra of a freshly prepared polymer film with a thickness of about 170 nm. Surprisingly, the ratio of the $\pi-\pi^*$ transition to the $\phi-\phi^*$ transition is decreased from 2.0 in solution, and the isotropic melt to a value of about 0.52 in the film. This indicates a very strong out-of-plane orientation of the (*E*)-azobenzene groups already in the freshly prepared film. Comparing a large number of films, the value varied from 1.0 to 0.3. The weak hypsochromic shift of the maximum indicates the beginning of the H aggregation. While the aggregation becomes much stronger, caused by aging at room temperature, or much faster, upon annealing at 70 °C, the homeotropic alignment is only slightly enhanced. However, smectic layering was detected by X-ray reflection exclusively after annealing[20] or UV irradiation. The smectic layering caused by the out-of-plane aligned azobenzene moieties seems to be stimulated by aggregation and vice versa. However, Figure 3 demonstrates that there is no direct correlation between both processes. For instance, the azobenzenes characterized by Figure 3a are more strongly oriented out-of-plane, but they are much less aggregated in the case of Figure 3b.

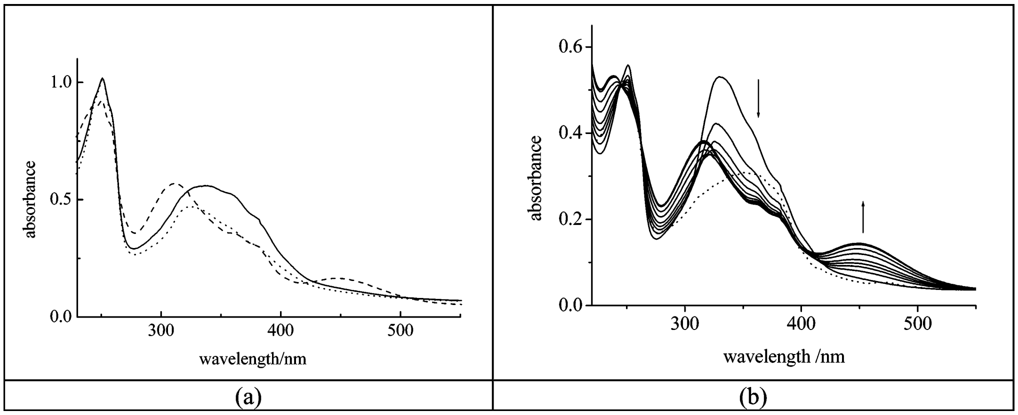
The UV irradiation results in similar spectral changes (Figure 3a and b) as in solution. However, in contrast to solution, isosbestic points are neither observed during the photoisomerization (Figure 3b) nor during the thermal *Z*/*E* isomerization. Therefore, the interpretation of all spectroscopic observations becomes more difficult due to the simultaneous occurrence of photoisomerization, subsequent orientation, and aggregation.

The steady state in the films established due to UV irradiation is quite different compared to that in solution because much fewer *Z* isomers are formed in the films under the same irradiation conditions. This is probably caused by restrictions resulting in nonreactive sites. The experiments show that the number of photochromic moieties that can undergo the *E*/*Z* photoisomerization processes strongly depends on the history of the film. Therefore, much fewer *E* isomers can react in annealed films in which the azobenzene moieties are more perfectly homeotropically aligned and more strongly aggregated (Figure 3a). By comparing a number of films, the smaller photoreactivity can be qualitatively correlated with stronger aggregation and stronger out-of-plane orientation. Compared to the solution, the initial quantum yield of the *E*/*Z* photoisomerization is 16 times smaller in a freshly prepared film and 20 times smaller in the case of an annealed film. However, continued UV irradiation partially destroys the aggregates, a steady state with a higher amount of *Z* isomers is finally established, and the subsequent thermal isomerization results temporarily in a film with nonaggregated azobenzene moieties.

UV irradiation and subsequent thermal *Z*/*E* isomerization result in an increase of the out-of-plane orientation. The high order parameter of about 0.72 indicates the homeotropic alignment. This is in good agreement with the order parameter of about 0.78 found for films that were annealed at 70 °C. Both annealing and UV exposure results in the transition of a less-ordered spin-coated film into a lamellar smectic-ordered film with homeotropically aligned mesogenes.

Figure 4 illustrates the height histogram after UV irradiation and subsequent thermal *Z*/*E* isomerization observed by SFM.

Elongated domains with sharp and angular edges are observed in the surface topography. The homogeneous surface of the spin-coated film is transferred to a surface characterized by smectic islands with a spacing of about 3.5 nm. These domains are comparable to the highly ordered smectic domains induced by annealing above the glass transition temperature. In both cases, the steps on the surface are in agreement with the spacing of the smectic layers found in the bulk and detected by X-ray reflectivity.[19]



(a) (b)

Figure 3. UV−Vis absorbance spectra of spin-coated films (a) after spin-coating (—), after annealing (···), and after subsequent nonpolarized UV irradiation (---) ($\lambda_{ex} = 365$ nm, $P = 7$ mW cm^{-2}). (b) Upon nonpolarized UV irradiation of a fresh-prepared film (—) ($\lambda_{ex} = 365$ nm, at 0, 1, 2, 5, 10, 20, 60, 120, 300, and 600 s, $P = 7$ mW cm^{-2}) and after *Z*/*E* isomerization (···).

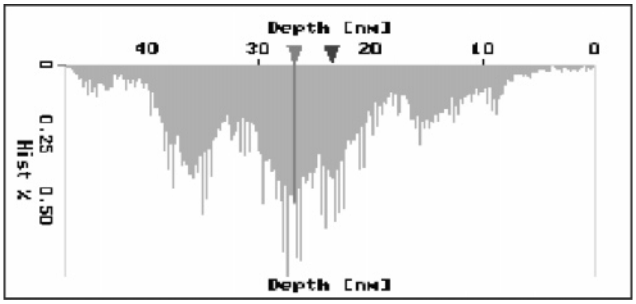


Figure 4. Height histogram after nonpolarized UV irradiation and subsequent thermal *Z*/*E* isomerization observed by SFM (λ_{ex} = 365 nm, *P* = 7 mW cm^{-2}).

By supplying energy due to annealing or irradiation, the nonequilibrium state of the spin-coated film is transferred to the layered morphology of the smectic polymer, changing the surface topology as well.

Change of the Orientational Order upon Irradiation with LP Visible Light. Films of different thickness and history were studied in order to answer the question whether the orientational order of the azobenzene moiety as part of the main chain can be modified by photoorientation irradiating with linearly polarized visible light.

As discussed above, the initial films are characterized by a different degree of out-of-plane orientation of the azobenzene groups, but the in-plane component is isotropic (Figure 5a). The polar plots in Figure 5 show the angular absorbance of the azobenzene moieties at 325 nm before (a) and after (b) the irradiation with linearly polarized light. The propagation direction of the laser light corresponded with the normal of the film. The absorbance was measured at different positions of the polarizer (each 10°). Figure 5 demonstrates that the irradiation with linearly polarized green light results in a preferred orientation of the azobenzene moieties perpendicular to the electric field vector of the incident light. In this way, the concentration parallel to the electric field vector $\vec{E}$ becomes lower and, simultaneously, perpendicular to $\vec{E}$ becomes enriched as they cannot be excited anymore.

As shown, the irradiation of an isotropic film in the normal results in an oblate order in which the azobenzenes become oriented in a plane perpendicular to $\vec{E}$. The question arises how the layered structure of the more or less homeotropically aligned and H-aggregated azobenzene moieties influence the light-induced orientation process. Surprisingly, high values of the dichroism up to 0.43 (Figure 5b) are induced in freshly prepared films of thickness between 50 and 300 nm at room temperature. However, the photoinduced dichroism becomes smaller in films with more pronounced out-of-plane order and stronger H aggregation. Thus, a dichroism of only 0.09 is generated in an ordered film, which was annealed at 70 °C for 30 min. Figure 6 presents the correlation between the saturation values of the photoinduced dichroism and the initial out-of-plane order parameter of the films. The dichroism generated by the photoorientation process is significantly decreased with increasing order and aggregation. A similar behavior was found in the case of aligned films of LC side-group polymers and LB multilayers,[9,28,40] where the photoreorientation process of aligned azobenzene moieties is drastically restricted by order and aggregation. In general, it is difficult to discriminate between the contribution of aggregation and of the orientational order concerning this restriction. In contrast to LC side-chain polymers, the restriction in the main-chain polymer under investigation cannot be overcome by an intermediate UV irradiation to transfer the film into a less-ordered and de-aggregated state. Caused by the dense packing, UV exposure cannot destroy the formed aggregates in the case of the main-chain polymer.

It is surprising that the photoorientation of the azobenzene group of this main-chain polymer results in such high values of photoinduced anisotropy. There is no significant restriction of the orientation process of the photochromic group incorporated in the polymer backbone compared to side-chain polymers with the same photochromic group and hexamethylene spacers as well. Possibly, the specific supramolecular structure of the polymer forming smectic layers with a number of hairpins in the backbone is the reason for this behavior. In such arrangement, the azobenzene groups can be driven by a movement like on a cone, modifying the in-plane orientation component.

Temperature Stability of the Induced Anisotropy. Because of photoorientation, a dichroism of about 0.27 was induced in a film at 20 °C. Simultaneously, the average absorbance is decreased from 1.18 to 0.9, as shown in Figure 7. This is caused by two processes: first, because of establishing the steady state of the photoisomerization at 458 nm and, second, by the increasing out-of-plane component due to the photoorientation process aligning more and more azobenzene groups in the propagation direction of the polarized light.

We have demonstrated that the anisotropy photoinduced in films of LC side-chain polymers can be amplified by thermotropic self-organization of the polymer due to annealing in the mesophase.[36,41−45] Depending on the spatial order, interfacial interactions, and the ordering tendency of the polymer, it can result in a stronger in-plane order or in a homeotropic alignment. But how does it work in the case of this main-chain polymer? To answer this question, the sample was annealed in steps of 10 °C, holding each temperatures for 20 min and measuring dichroism and average absorbance (Figure 7). Both values remain nearly constant in the glassy state and in the S_B phase. However, the dichroism falls down dramatically to a level of 0.1 at 54 °C, which corresponds to the phase transition $S_B \rightarrow S_A$ in the bulk. It then exhibits a plateau and vanishes at the clearing point. Simultaneously, the average absorbance increases from 0.8 to 1.7. This value was kept constant between 70 and 80 °C, falls down to 0.65 at 110 °C, and increases again to 2.1 at the clearing point. Caused by this unique development of the absorbance characterized by a maximum and a second minimum, it becomes clear that it cannot be a simple isotropic melt. Using the values for the isotropic melt above T_{cl} and the aligned state at 110 °C, an out-of-plane order parameter of 0.7 is calculated by using the procedure described. By cooling down from the isotropic melt to room temperature, a small dichroism of about 0.05 and an absorbance of 0.80 were found, which corresponds to a degree of out-of-plane order of 0.63.

The temperature dependence of the absorbance detected for the photooriented sample is quite similar to that of a film that was just annealed without any irradiation.[20]

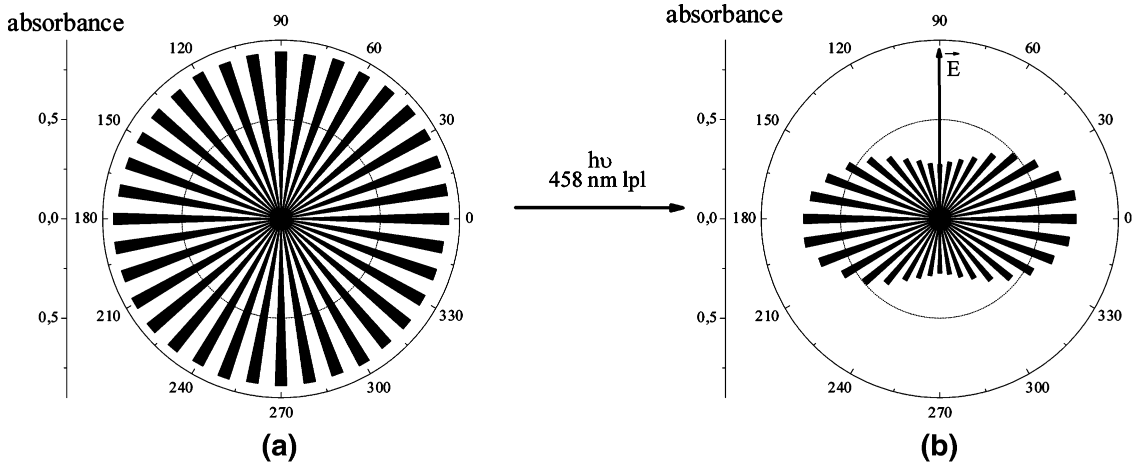


Figure 5. Angular-dependent absorbance of a polymer film at the maximum of the $\pi-\pi^*$ transition before (a) and after (b) irradiation with linearly polarized light ($\lambda_{ex} = 458$ nm, $P = 50$ mW cm^{-2}).

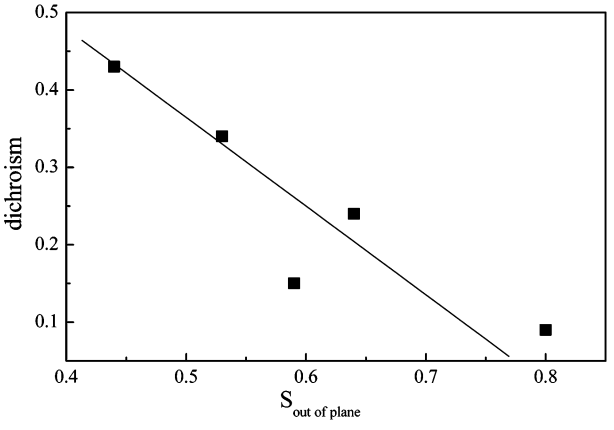


Figure 6. Relation of the photoinduced dichroism and the initial out-of-plane order.

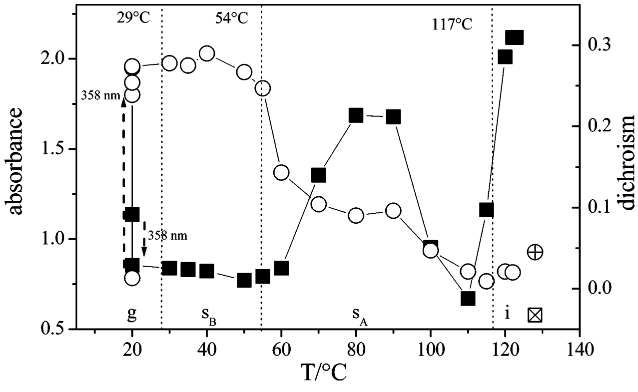


Figure 7. Change of dichroism (circle) and average absorbance (square) of linearly polarized irradiated film upon annealing ($\lambda_{ex} = 458$ nm, $P = 50$ mW cm^{-2}). The temperature is kept at each point for 20 min. Value after cooling (squared cross, average absorbance; circled cross, dichroism).

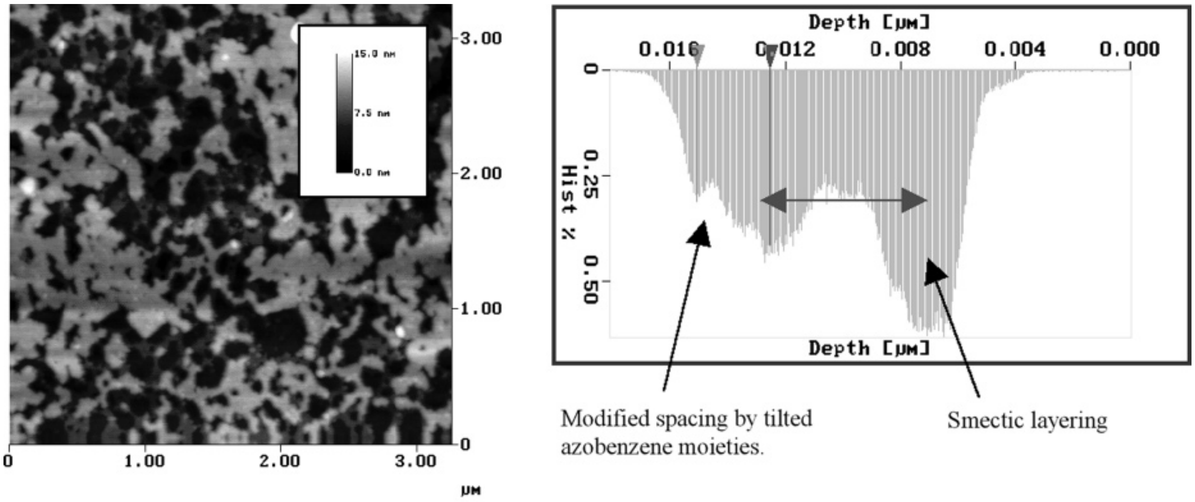
Subsequent annealing at temperatures of the S_B and S_A phase of the films results in the formation of smectic layers, connected with a decrease and a hypsochromic shift of absorbance caused by homeotropic alignment and aggregation. But upon annealing at 80 °C, a significant increase of the absorbance is observed exactly up to the level that is characteristic for the isotropic films. The out-of-plane orientation of the chromophores was visualized by the inspection of the sample at an angle of 45° to the normal. This unique behavior cannot be explained by the reported sequence of a mesophase. All results are in agreement with the formation of an isotropic mesophase between the S_B and S_A phase. Isotropic LC phases, e.g., cubic phases, smectic D, or TGB, can be formed between two other mesophases.[46−50]

The self-organization process takes place independent of the light exposure or the photoinduced order. In all cases, the photoanisotropic films are transferred to an isotropic one by annealing, whereas the supramolecular structure of the new phase is not obvious and requires further investigation.

Light-Induced Change of the Surface Topology. A spin-coated, aged film of about 9 nm thickness deposited on a silicon wafer, detected by SFM, exhibits the smectic island topology as described. The thickness of the top layer deduced from the height histogram is about 3.5 ± 0.5 nm. The islands have the same thickness as the spacing of the smectic layers in the polymer bulk as detected by X-ray reflection, indicating that the film interface polymer−air is formed by a homotropically aligned layer of the LC polymer.

However, irradiating this film with linearly polarized light of 488 nm and characterizing the film surface after the thermal *Z*/*E* isomerization, the histogram shows a second peak (Figure 8) corresponding to a height of about 2.1 ± 0.5 nm. The height corresponds to a layer of tilted (*E*)-azobenzene units with a tilt angle of about 50°. The signal at 2.1 nm disappears upon annealing of the film at 70 °C for 6 h, rebuilding the height of 3.5 nm. The SFM inspection after a second irradiation procedure with linearly polarized light shows the recreation of the spacing of 2.1 nm again. Angular-dependent UV−vis spectra of another film on silica glass makes clear that the irradiation with linearly polarized light results in an orientation of the azobenzene units in such a way that the out-of-plane orientation is preserved or even improved, but simultaneously, the projection of the absorbance on the plane exhibits an angular maximum perpendicular of the electric field vector of the incident light. This corresponds to the model of tilted layers caused by the photoreorientation of the photochromic moieties such as a movement on a cone.

Photoorientation of a Dewetted, Ultrathin Film. It was shown recently that an ultrathin film with a thickness of 5 nm exhibits a completely different behavior upon annealing. In contrast to thicker films, it dewets, forming a regular network of rims and holes,



(a) (b)

Figure 8. SFM image of the surface topography of a thin film after irradiation with linearly polarized light at 458 nm. (a) Topographic image, (b) height histogram.

whereas a planar aligned monolayer covers the substrate between the volcano-like rims formed by smectic layers. The fact that there is no contrast in the phase image between the rims and the holes demonstrates clearly that the holes are covered with the polymer. It is an interesting question whether the azobenzene moieties can be photoreoriented in such a dewetted structure.

The irradiation with linearly polarized light carried out under the same conditions results only in a very small dichroism of approximately 0.05. As aspected, the maximum absorbance is found perpendicular to $\vec{E}$. The induced anisotropy is 1 order of magnitude smaller compared to the dichroism induced in thicker films. Caused by the heterogeneous structure of the film, it cannot be distinguished which part of the structure was photooriented. So far, the reason of the restriction it is not clear. Probably, it could be caused by the interfacial interactions of the planar aligned polymer to the substrate or, alternatively, it could be caused by the changed organization of the polymer backbone, which is transferred from a microsegregated lamellar structure with hairpins into the backbone and homeotropically aligned azobenzene moieties to an elongated planar-aligned backbone.

IV. Conclusion

Two photoinduced ordering processes in thin films of a photochromic liquid crystalline main-chain polymer were studied by using nonpolarized UV and linearly polarized visible light. Already, as a result of the spin-coating process, the smectic polymer starts to undergo a spontaneous self-ordering process, which becomes more perfect on storage at room temperature, annealing above T_g, and upon UV irradiation at room temperature. The out-of-plane order of the azobenzene groups is established quite fast and becomes only slightly more pronounced by annealing or UV irradiation, resulting in a homeotropic alignment of the azobenzene groups.[16,23] Contrary to that, the H-aggregation of the azobenzene moieties caused by $\pi-\pi$ stacking and the formation of lamellar order established parallel to the interface polymer−air requires more time or a higher mobility. This was achieved by annealing in the mesophase.[20] The study shows that the ordering process can be enforced by UV irradiation and the subsequent thermal *Z*/*E* isomerization. While the thermotropic self-organization by annealing occurs at 70 °C in the S_A mesophase, the photoinduced ordering process takes place at room temperature. The process is caused by temporarily lowering the order and by the photoinduced dynamics in the steady state of the photoisomerization. Therefore, the nonequilibrium state of the spin-coated film is transferred to a macroscopically ordered film with smectic layers. In both cases, a higher molecular mobility is a necessary condition, allowing the polymer to relax to a more stable state.

The ordering process is more than a simple thermotropic self-organization of a liquid crystalline system resulting in any multidomain structure. The final films are optically clear, nonscattering ones characterized by a macroscopically ordered layer structure. The layering is caused by the different interfacial interactions of the chemically different segments of the polymer.

The supramolecular order established by thermotropic self-organization can be modified upon irradiation with linearly polarized light. In this way, the photochromic azobenzene moieties become oriented perpendicular to the polarization plane, preserving the layered structure. In the case of this layered system, the initial order is modified by the photoorientation process in such a way that the chromophores become tilted. Therefore, the layered structure remains intact, but an additional spacing of the top layer indicates that a part of the photochromic (*E*)-azobenzene moieties is tilted to the normal, forming an average angle of 50°. Therefore, these azobenzene moieties should move like on a cone, resulting in a dichroism of up to 0.43.

The photoorientation process of the dewetted ultrathin film is 1 order of magnitude less efficient compared to the photoinduced anisotropy of bulk films. The difference can be explained by the elongated backbone in the planar aligned monolayer and the stronger interactions of the polymer with the substrate.

In contrast to some LC side-chain polymers, the photoinduced order of the films cannot be amplified by annealing with respect to an optically isotropic mesophase.

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