Light-Induced Orientation Phenomena in Langmuir–Blodgett Multilayers

Th. Geue,[†] A. Ziegler, and J. Stumpe*

Institute of Chemistry, Humboldt-University Berlin, Erieseering 42, D-10319 Berlin, Germany

Received March 18, 1997; Revised Manuscript Received June 23, 1997[⊗]

ABSTRACT: The double-layer structure of Langmuir–Blodgett (LB) multilayer assemblies formed by a thermotropic polyacrylate with 2-hydroxyethyl and [[[[(2-methylbutyl)oxy]phenyl]azo]phenoxy]hexyl side groups is modified by annealing and on ultraviolet (UV) irradiation. Both procedures cause order–disorder transitions. The interaction with linearly polarized visible light results in a reversible reorientation of the azobenzene side groups maintaining the layered structure. In this way the optical anisotropy of the LB films is modified reversibly and continuously. In the original multilayer the photoreorientation process is restricted by the dense packing of the side groups. But the process takes place after weakening the intermolecular interactions. This has been achieved by a suitable preparation of the films, by annealing of the thermotropic polymer, or by a photochemically induced decrease of the supramolecular order. The photogeneration of anisotropy is governed by the molecular aggregation, the orientational order, the thermotropic ordering tendency of the polymer to establish a homeotropic alignment, and the irradiation conditions (wavelength, power density, polarization direction). Continued irradiation or annealing above the glass transition temperature (T_g) results in a decrease of absorbance indicating smaller tilt angles. The photoinduced dichroism is long-term stable but can be erased by irradiation and heating.

Introduction

Langmuir–Blodgett (LB) multilayer assemblies are distinguished by a vertical layered structure. The dipping process results in a tilted arrangement of the amphiphilic moieties, causing azimuthal anisotropy. It would be useful to be able to overcome domain structure and to reorient films after they have been deported as solid phase. This requires the introduction of molecular mobility into the LB multilayer by heating or illumination without destroying the layered order. The manipulation of LB order by external forces or photoreactions is of great interest. In the case of thermotropic polymers with photochromic azobenzene groups, this can be achieved by annealing[1] or irradiating.[2–13]

Upon irradiation the azobenzene moieties undergo *E–Z* photoisomerization (Figure 1) and a wavelength-dependent steady state is established between the rodlike *E* isomers and the bent *Z* isomers. Not only is there a change of the electronic structure, well-known as photochromism, but also simultaneously shape, polarity, and transition moment of the photochromic moiety are modified. These changes of the molecular structure result in modified intermolecular interactions and, in this way, in a modification of the supramolecular order of the LB multilayer. So, the periodicity of the lamellar architecture and the in-plane order is affected. Moreover, a sufficient disturbance usually led to a irreversible loss of the supramolecular LB structure.[14–17] To avoid this, LB multilayers built up of a thermotropic polymer have been studied as a reversible model.

The interaction of photochromic moieties with linearly polarized light offers a new way to orient such groups in polymer films and supramolecular assemblies.[18–31] In this way the optical properties of films may be changed by the photochemically induced modification of the orientational distribution. In the glassy state of
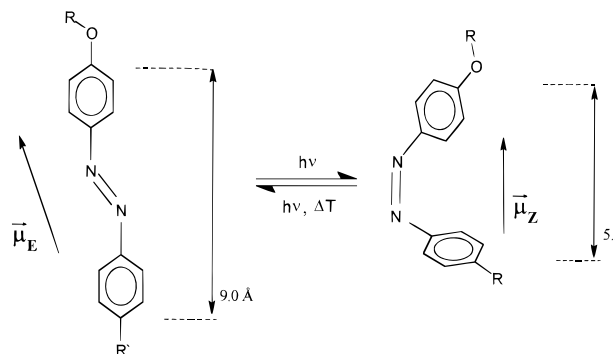

Figure 1. Photoisomerization of azobenzene.

polymers the photoorientation process results in long-term stable anisotropy. In this way optical anisotropy is generated in isotropic films of amorphous and liquid-crystalline polymers (LCP)[26,27] or the anisotropy of aligned LCP films is modified by photoreorientation.[25] Photoinduced anisotropy in LB films was shown by Barnik et al. for the first time in 1988.[19] Recently, photoreorientation was demonstrated in LB multilayers of polymers, such as thermotropic polyacrylates[2–5] and "hairy rod" polyglutamates.[9]

Different mechanisms are discussed for photoorientation process caused by irradiation with linearly polarized light.[25–27,32–40] In the case of azobenzene moieties it is mainly accepted that the repeated angular-dependent photoselection, photoisomerization cycles, and rotational diffusion within the steady state results in a photochemically induced directed reorientation of the photochromic moieties.[19–21,25–27] The probability for the excitation of an individual (*E*)-azobenzene chromophore follows to $\cos^2 \omega$, where ω is the angle between the electric field vector of the incident light and the transition moment of the photochromic moiety which coincides approximately with its long molecular axis. Thus, molecules oriented parallel to the electric field vector preferably undergo the photoreaction (angular-dependent photoselection). After an isomerization cycle, the site and the orientation of a rebuilt *E* isomer is changed. As a consequence, an increased angle ω decreases the

* Author to whom the correspondence should be addressed.
[†] Present address: Institute of Solid State Physics, University of Potsdam, Am Neuen Palais 10, D-14469 Potsdam, Germany.
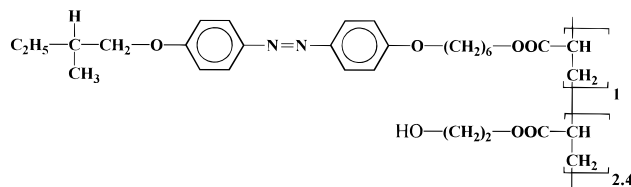[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

Figure 2. Copolyacrylate with alkoxyazobenzene and hydroxyethyl side groups.

probability of repeated excitation. In this way the photochromic moieties will be continuously reoriented toward a direction perpendicular to the electric field vector of the incident light. The established orientational order remains stable in the glassy state, whereas the photochromic moieties are restored on the molecular level.

The influence of the initial order on the process is somewhat controversially discussed. On the one hand, it was shown recently that the photoreorientation process can be restricted by the initial order of aligned LCP films and LB multilayers.[9,25] In such ordered systems the photoisomerization takes place but the photoreorientation process is suppressed by the liquid-crystalline order. On the other hand, very recently, a different model was proposed in which the initial order of LB multilayers or liquid crystals plays an essential role for the light-stimulated reorientation process.[32-40]

LB multilayers and spin-coated films of the same thermotropic polymer, a 2-hydroxyethyl polyacrylate with alkoxyazobenzene side groups, are an interesting and reversible model system to study the photo(re)-orientation processes depending on the supramolecular order.[2-5] The polymer combines the ability to form LB multilayer assemblies and to undergo thermotropic self-organization.[1] Upon UV irradiation the initial double-layer structure is irreversibly destroyed by the *E-Z* photoisomerization connected with a loss of the initial in-plane anisotropy. A new layered structure with modified spacing and without any macroscopical optical in-plane anisotropy was generated by subsequent visible (Vis) irradiation. Very recently, it was shown[2,4,5] that on irradiation with linearly polarized light the tilted azobenzene side groups were reoriented, yielding optical in-plane anisotropy with an azimuthal angle of 90° toward the electric field vector of the incident light, while the layered structure was maintained.

The aim of this contribution is to study the photo-(re)orientation process and the stability of photoinduced optical anisotropy in LB multilayers and spin-coated films of a smectic polymer depending on the irradiation conditions and the state of order established via the temperature or by irradiation.

Experimental Section

Photochromic Langmuir–Blodgett multilayers of the copolymer consisting of 2-hydroxyethyl acrylate and [[[[(2-methylbutyl)oxy]phenyl]azo]phenoxy]hexyl acrylate (Figure 2) were prepared by means of the Langmuir–Blodgett–Kuhn technique.[1] The amphiphilic copolymer exhibits liquid-crystalline behavior in the bulk (g 30 k 56 s 86 i).[1]

Stable monolayers were obtained at 20.7 °C in a KSV 5000 trough on pure water (Milli-Q system) by spreading a 1×10^{-3} M chloroform solution and extremely slow compression at about 5 cm²/min. Surface pressure readings were performed with a Wilhelmy plate.

Transfer of the monolayers onto hydrophobic quartz plates was carried out at a dipping speed of 5 mm/min and a surface pressure of $\pi_0 = 33$, 36, or 39 mN/m. Transfer ratios of both up and down strokes were above 0.94. To keep the dark

adapted material in the *E* configuration, care was taken by working in the absence of actinic light.

The spin-cast films were prepared using a solution of 2% by weight in chloroform and spun at 1000 rpm on silica glass substrates. The films were dried in an oven at 40 °C under vacuum for about 30 min in order to remove the rest of the solvent.

The polarized UV/Vis spectra were measured on a Lambda 19 spectrometer (Perkin-Elmer) equipped with a set of Glan–Taylor prism polarizers made of calcite (LOT). The self-designed polarization kit performs a 360° angle scan. The wavelength-dependent absorption data were extracted from the polarized and angular-dependent UV/Vis spectra series and plotted in polar coordinates as the vector length of the absorbance at a given wavelength vs the polarizing angle of the incident light beam. Thus, the polar diagrams represent the azimuthal projection of the distribution function caused by the $n\pi^*$ and $\pi\pi^*$ transition moments of the (*E*)-azobenzene chromophores which coincide approximately with the long molecular axis of the (*E*)-azobenzene chromophores.

The minimum and maximum of the angular-dependent absorbance yield a dichroic ratio by $R = A_{max}/A_{min}$. The dichroism was calculated by $D = (A_{max} - A_{min})/(A_{max} + A_{min})$, where A_{max} = maximum absorbance and A_{min} = minimum absorbance perpendicular to A_{max}.

Irradiations were carried out by a mercury HBO 500 lamp and appropriate filters on a conventional optical desk as well as by an Innova 90 Ar⁺ laser system (Coherent) at 357, 457.4, and 488 nm.

Results

Optical Properties of Differently Ordered Films on Irradiation with Nonpolarized Light. On irradiation the azobenzene moieties of the polymer undergo *E-Z* photoisomerization in solution, spin-coated films, and LB multilayers. The established steady state between both isomers depends on the ratio between the absorbance coefficients of the *E* and *Z* isomers at the excitation wavelength as well as on the molecular environment of the chromophores.

The change of the absorption spectrum on irradiation of the polymer in chloroform with UV light (365 nm) is shown in Figure 3A. Figure 3B illustrates the different steady states on irradiation at 365 and 436 nm. Upon UV irradiation the steady state is characterized by a high ratio of the *Z* isomers, while in the case of the Vis irradiation the rodlike *E* isomers dominate. Figure 3B demonstrates that the thermal *Z*–*E* isomerization results in the re-creation of the initial absorbance.

Figure 4 compares the spectra in chloroform with those of a spin-coated film and a LB multilayer after different procedures. In both types of films the symmetric shape of the $\pi\pi^*$ band becomes asymmetric at the initial states. The maximum of absorbance in solution at 359 nm is shifted to 328 nm in the spin-coated film and the multilayer. Both facts indicate an excitonic interaction of the aromatic chromophores forming H-aggregates. The (*E*)-azobenzene chromophores should be arranged "face to face" in dimers or higher aggregates. The process can be described qualitatively by the exciton model introduced by McRae and Kasha.[41] A publication about this subject in different ordered films of the polymer is in preparation.

The difference of the spectra after UV irradiation shows that different steady states are established. This is due to the different molecular environments of the azobenzene moieties in both types of films and in solution. In all cases the subsequent Vis irradiation results in a state with a small content of *Z* isomer. In solution the initial absorbance is achieved by the thermal *Z*–*E* isomerization. The UV/Vis irradiation
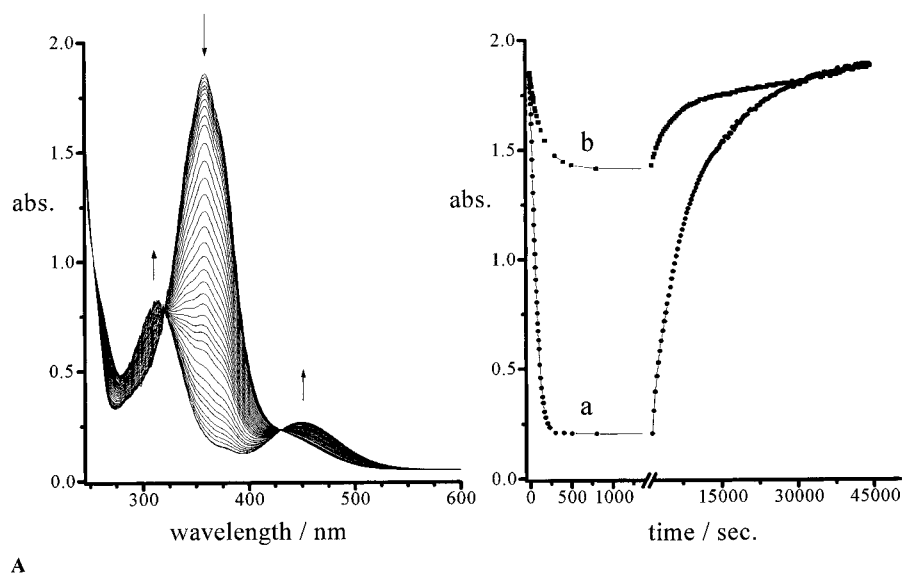
Figure 3. (A) Change of the spectra of the polymer in chloroform on irradiation (λ_{ex} = 365 nm, P = 2.5 mW/cm^2). (B) Absorbance at 365 nm versus the time irradiating with 365 (a) and 436 nm (b) and subsequent thermal $Z-E$ isomerization in the dark.
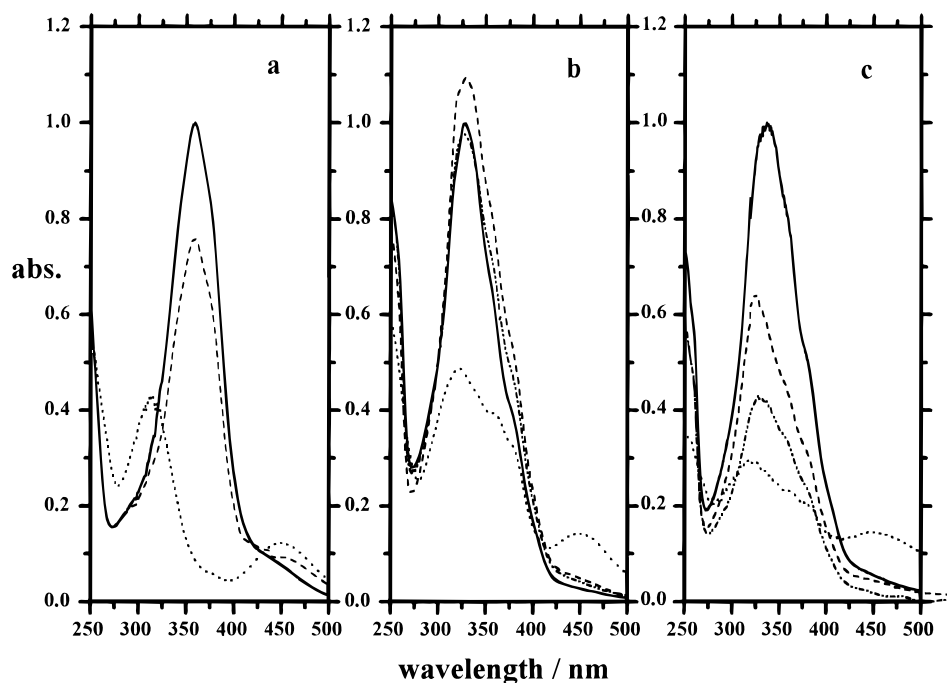

Figure 4. Normalized absorbance of the polymer in chloroform (a), as a spin-coated film (b) and as a LB multilayer (c) (144 double layers) in the initial state (−), after UV irradiation (365 nm) (···), after subsequent Vis irradiation (457 nm) (− −), and relaxation at room temperature (16 h) (−··−).

cycle of the spin-coated film yields to a bathochromically shifted and higher $\pi\pi^*$ absorbance compared to that of the initial film. This indicates the conversion of H-aggregation species to nonaggregated E isomers by the isomerization cycle.[13] But the $\pi\pi^*$ absorbance decreases to the initial value by reaggregation during 16 h. The simultaneously observed decrease of $n\pi^*$ absorbance indicates the continued occurrence of the $Z-E$ isomerization, but the expected increase of the $\pi\pi^*$ absorbance is overcompansated by the reaggregation process. However, in the case of the LB multilayer the irradiation cycle results in a much larger change of absorbance. In the LB multilayer the absorbance is decreased to approximately 50% of the initial value and does not reach that of the virgin LB multilayer anymore (see also Figure 6). The short wavelength of the maximum and the decrease of absorbance indicate the aggregation and

a decreasing tilt angle of the azobenzene side groups. This strictly corresponds to the structure model proposed from the X-ray reflection and grazing incidence diffraction measurements.[2−8]

So, the decreased absorbance is in agreement with the increased spacing of 46−52 Å.[8] Simultaneously the optical in-plane anisotropy caused by the tilted side groups oriented toward the dipping direction gets lost as shown in Figure 6. Moreover, the decrease of absorbance is continued on storage in the dark by the formation of H aggregates and the improvement of the homeotropic alignment. In this way the initial strained LB multilayer is transformed into a less ordered structure. This behavior of the thermotropic polymer was characterized as an order−disorder transition caused by the conversion of the LB structure to a liquid-crystalline lamellar order which is similar to that of the bulk.[1−8]
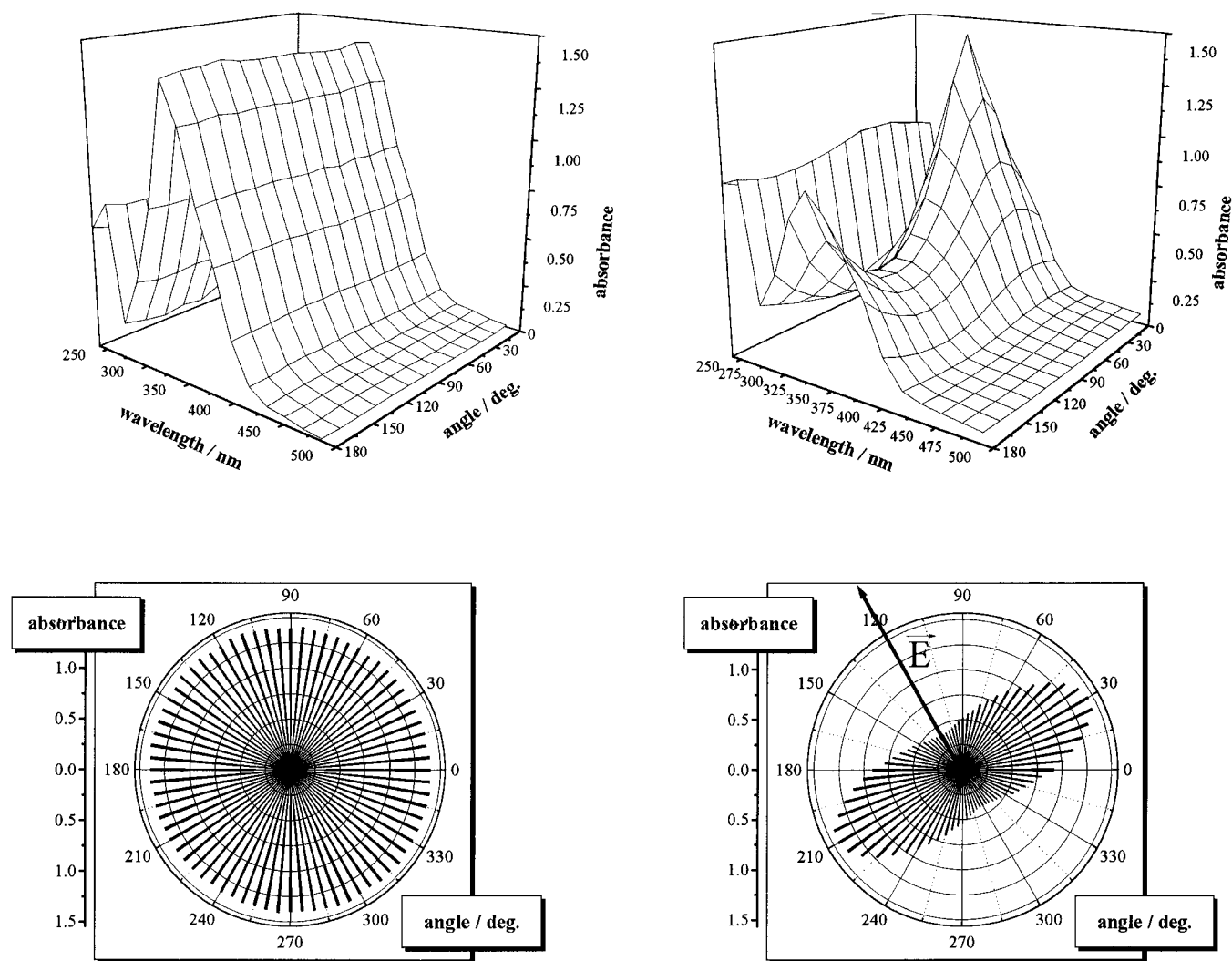
Figure 5. Angular-dependent spectra and angular-dependent absorbance at 330 nm of the spin-coated film before and after irradiation with linearly polarized light ($\lambda_{ex} = 457$ nm, $P = 20$ mW/cm^2). $\vec{E}$ indicates the electric field vector.

Photoorientation of Spin-Coated Films. Upon irradiation with linearly polarized Vis light (457 nm, 2 mW/cm^2) optical anisotropy is induced in optically isotropic spin-coated films. The linearly polarized light generates an orientation of the azobenzene moieties perpendicular to the direction of the electric field vector of the incident light. This orientation process proceeds on continued irradiation within the steady state. This is demonstrated by the dichroism of the $\pi\pi^*$ transition as shown by the angular-dependent spectra in Figure 5. The polar diagrams for the same film before and after the exposure illustrate the change of the angular distribution of the absorbance at 330 nm in more detail. The photoinduced dichroism is 0.56. This is remarkably high compared to that of other LC polymers with azobenzene side groups. Below the glass transition temperature the induced orientational order of the film remains stable for months.

Polarized Irradiation of the Original LB Multilayers. The original LB multilayers exhibit different values of dichroism from 0.16 up to 0.63 at the depicted wavelength of the maximum absorbance at 335 nm depending on the preparation conditions. Hereby, the side groups are arranged in layers of different tilt angles but always directed toward the dipping direction caused by the transfer process. The spacing of the layer and the corresponding in-plane order can be modified by the

transfer pressure. The low-ordered LB multilayers are prepared at 33 mN/m and the high ordered films at 39 mN/m. The azimuthal absorbance of the chromophore is shown in Figure 6 for the initial state of a high-ordered LB multilayer.

The irradiation of the multilayer using linearly polarized Vis light (436 nm, 2 mW/cm^2, with an angle of 45° with respect to the initial orientational direction) decreases slightly the dichroism but does not result in a change of the orientational direction. This fact is in contrast to the behavior of the spin-coated film. It is assumed that the photoreorientation of the azobenzene moieties is suppressed by the dense packing of the LB structure. Upon irradiation with nonpolarized Vis light the absorbance is decreased slightly as well but the orientational direction and the dichroic ratio remain preserved. The photochemical disturbance caused by the procedure under these conditions (wavelength, power density, temperature) is not high enough to overcome the initial LB order.

However, the reorientation takes place using a higher power density (20 mW/cm^2). The axis of azimuthal dichroism is shifted only by an angle of 30°. The theoretically expected value of 45°, i.e., 90° with respect to the E vector, is not established. This is typical for an incomplete reorientation process. The dichroism (0.49) in the new direction is less compared to the
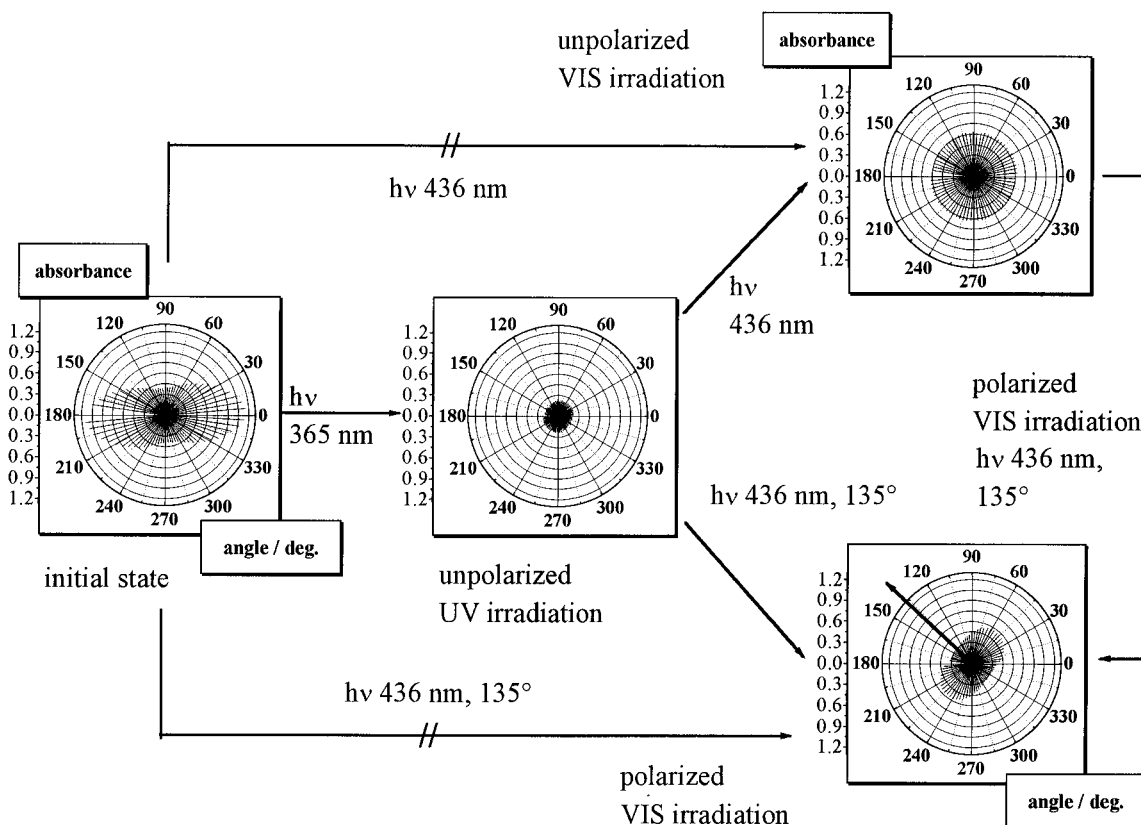
Figure 6. Light-induced erasure and induction of optical in-plane anisotropy: Angular-dependent absorbance of LB multilayer (64 layers) on UV and Vis irradiation at 20 °C. The electrical field vector of linearly polarized irradiation is illustrated as arrow in the polar diagram.

primary state. Simultaneously the average absorbance decreases to 0.64 of the initial value. This may be due to the connection of the photoreorientation changing the in-plane dichroism and the vertical ordering tendency of the side groups. The reason for the dependence of the photoreorientation process on the power density is not clear yet. It is suggested that the molecular environment of the chromophores is locally and temporarily heated. Nevertheless, such a threshold of the photoreorientation process caused by the supramolecular order is of major interest.

However, an efficient photoreorientation process takes place on irradiation even with low power density (2 mW/cm²) in a less ordered multilayer ($D = 0.16$). In this case a shift of the angular-dependent maximum of absorbance is induced perpendicular to the polarization plane, indicating a complete reorientation process. But the photoinduced dichroism is comparatively small. Due to the same wavelengths of the high- and less-ordered films, the molecular aggregation of the azobenzene side groups should be similar in both multilayers. This suggests that the strong orientational order of the side groups is responsible for the restriction within the high-ordered multilayer rather than the molecular aggregation.

The modification of optical anisotropy depends not only on the power density but also on the wavelength of the incident light. So, the irradiation of the LB multilayers with linearly polarized UV light (365 nm) does not result in the generation of optical anisotropy. The initial order is destroyed, but the disturbance caused by the Z isomers at this steady state is so high that a new orientational order cannot be generated. The irradiation with nonpolarized UV light (365 nm) leads to a similar isotropic film without in-plane orientational

Table 1. Multistep Photoreorientation Procedure of a Highly Ordered Multilayer at Room Temperature after UV Irradiation[a]

	$\gamma_{P,436\ nm}$ (deg)	α (deg)	β (deg)	$\Delta\psi$ (deg)	D	average abs.$_{335\ nm}$
a	135	isotropic[b]	45	b	0.34	0.42
b	30	45	120	75	0.39	0.40
c	95	120	185	65	0.44	0.34
d	225	185	135	50	0.34	0.38

[a] Angle of the maximum of absorbance (335 nm) of aligned film before (α) and after (β) irradiation with linearly polarized light with an angle of the E vector γ_P (436 nm, $P = 1.64$ J/cm²) in laboratory coordinates, where the reorientation angle is $\Delta\psi = \beta - \alpha$. [b] The photoinduced orientational direction is always 90° with respect to the polarization plane (γ) for isotropic films.

order of the side groups. The subsequent nonpolarized Vis irradiation rebuilds the E isomers and results in an isotropic distribution of absorbance.

Photoreorientation of LB Multilayer after Photochemical Decoupling of Initial Order. In order to change the direction of optical anisotropy in high-ordered multilayers by means of linearly polarized light with low power density (2 mW/cm²), it is necessary to destroy this primary orientational order and the molecular aggregation. This can be done by UV irradiation or an UV/Vis photoisomerization cycle. Both procedures result in optically isotropic films but different ratios of E and Z isomers. The subsequent polarized Vis irradiation (1.4 J/cm²) generates a new orientational direction combined with a new orientational distribution of the chromophores (Figure 6).

On irradiation at an angle of 135° with respect to the primary, but now erased orientational direction, which corresponds to the dipping direction, the maximum absorbance was found to be in the direction of 45°, i.e.,
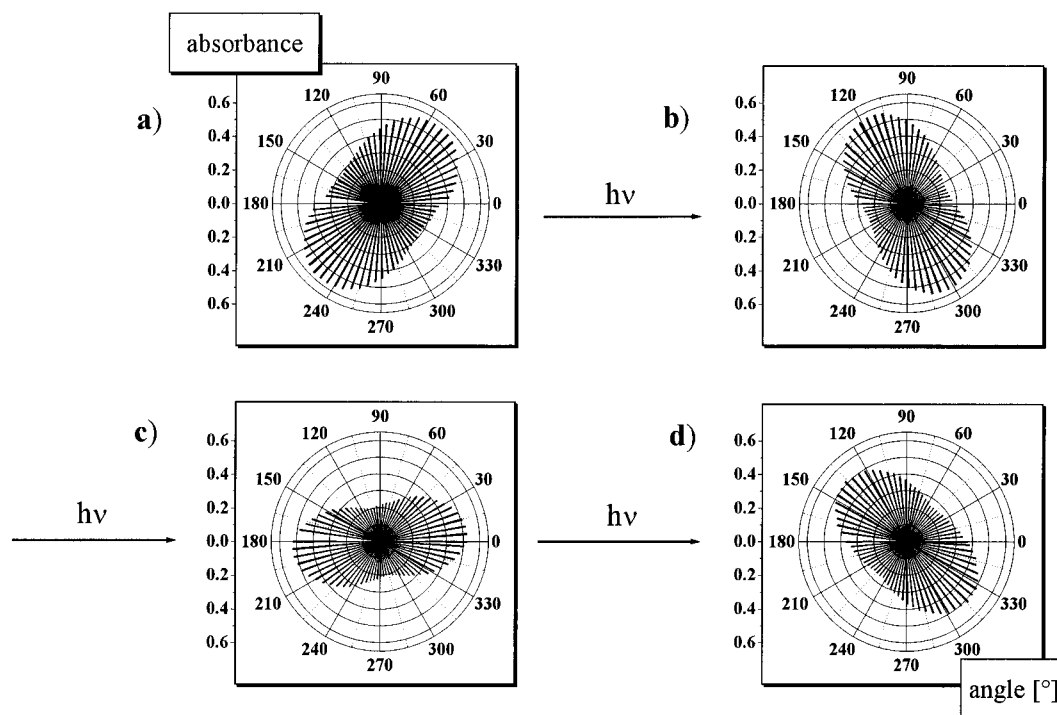
Figure 7. Multistep photoreorientation: Change of the angular-dependent absorbance of a LB multilayer at 335 nm on polarized irradiation (λ_{ex} = 436 nm, 2 mW/cm², P = 1.64 J/cm²) with different directions of polarization (a) 135°, (b) 30°, (c) 95°, and (d) 45° at room temperature. The procedure starts after the UV/visible irradiation cycle.

90° inclined to the electric field vector of incident polarized beam as expected for the theory. The dichroism established by this process is about 0.45; i.e., it is smaller than that of the virgin multilayer. An X-ray study has recently shown that a new layered structure with increased spacing of 52 Å is established by this procedure, which is the same resulting from nonpolarized Vis exposure.[3]

A second polarized Vis irradiation (2 mW/cm² with an angle of 45° between the induced orientational direction and the direction of the E vector) does not result in a further reorientation. The photoinduced orientation order of the film (D = 0.45) restricts the further reorientation (Table 4). But the process can be induced after an additional UV step or irradiation with Vis light of higher power density.

However, the polarized irradiation of a film with slightly smaller in-plane orientational order (D = 0.34) results in a reorientation (Table 1). This demonstrates a sophisticated dependence of the photoreorientation on the order. As reported in Figure 7, after UV irradiation dichroism (0.34) is photogenerated (step a). In step b the direction of the optical axis is changed upon irradiation with a different angle of the E vector of the incident light with respect to the sample. Apart from the polarization plane, a complete reorientation (steps c and d) is always observed. This results in an azimuthal rotation of the direction of dichroism under preservation of the layered structure. The reorientation angles $\Delta\Psi$, the dichroism values D, and the average absorbance are summarized in Table 1.

The reorientation angles $\Delta\Psi$ differ because of the different angles between the initial axis of dichroism and the direction of the E vector. It results always in a complete reorientation perpendicular to the incident beam. The photoinduced dichroism is similar for all steps. It is interesting that the highest value is reached for the orientation close to the former dipping direction. This suggests a memory effect of the original LB film.
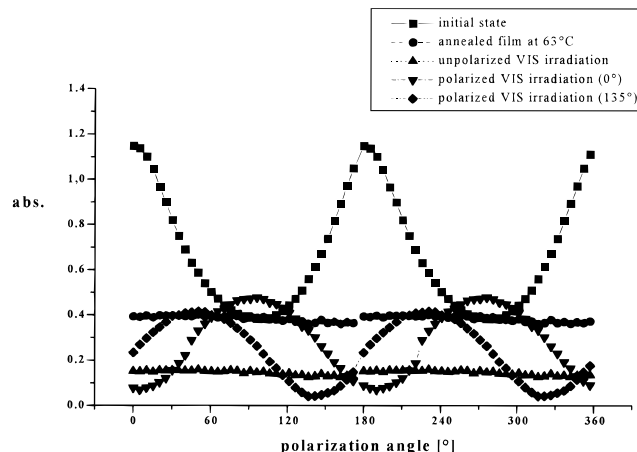

Figure 8. Light-induced erasure, induction, and modification of optical in-plane anisotropy: Angular-dependent absorbance of a LB film with 64 layers at 335 nm and at 56 °C. The linearly polarized irradiation procedure was carried out at 0° and a second step at 135° (436 nm, 2 mW/cm²).

The average absorbance is decreased by this multistep reorientation procedure, indicating that the number of homeotropically aligned chromophores increases.

Photoreorientation at Higher Temperatures. The annealing of the multilayer in the smectic mesophase (63 °C) causes a phase transition of the LB structure to the liquid-crystalline order.[8] This results in an increase of the spacing, a related decrease of absorbance, and the erasure of the optical in-plane anisotropy (Figure 8).

Polarized Vis irradiation (436 nm) does not induce optical anisotropy. The photoreorientation process is suppressed by the homeotropically aligned side groups and their cooperative dynamics in the smectic mesophase. The liquid-crystalline order affects the relaxation of the Z isomers and that of photooriented (E)-azobenzene side groups to reduce the photoinduced disturbance of the system.

Table 2. Change of the Photoinduced Dichroism (335 nm) on Thermal Fading at 56 °C[a]

	t_{relax} (min)	α (deg)	D	average abs.$_{335\ nm}$
a	0	45	0.82	0.24
b	30	45	0.63	0.25
c	60	45	0.35	0.30
d	120	45	0.27	0.25

[a] Initial exposure with Vis light (436 nm, 2 mW/cm^2, 56 °C). t_{relax} represents the time after switching-off the light.

Table 3. Photoinduction of Dichroism in LB Multilayers in Dependence on Temperature and Different Angles of the E Vector of Incident Light with Respect to the Sample[a]

	T (°C)	$\gamma_{P,436\ nm}$ (deg)	α (deg)	β (deg)	$\Delta\psi$ (deg)	D	average abs.$_{335\ nm}$
a	20	45	isotropic	135		0.34	0.38
b	56	135	135	45	90	0.82	0.24
c	56	0	45	90	45	0.74	0.29
d	20	30	90	120	30	0.29	0.30

[a] Angle of the maximum of absorbance (330 nm) before (α) and after (β) irradiation with linearly polarized light with an angle of the E vector γ_P in laboratory coordinates, where $\Delta\psi = \beta - \alpha$ is the reorientation angle.

However, a very strong dichroism is photogenerated in the same film and an identical orientational order at approximately 56 °C. The change of the angular dependence of absorbance is shown in Figure 8. The original multilayer exhibits a dichroism of $D = 0.63$ at room temperature. Annealing at 63 °C causes loss of the anisotropy and results in a decrease of the average absorbance. A further decrease of the isotropic absorbance is caused by establishing the steady state on nonpolarized Vis irradiation (436 nm). Starting from this film, the linearly polarized irradiation at 56 °C generates a dichroism of 0.81, with the maximum absorbance perpendicular to the polarization direction of the incident light. Thus, in this small temperature range of some degrees Centigrade a drastic change of the photoorientation behavior is observed. The temperature of 56 °C is close to the phase transition crystalline/smectic of the polymer in the bulk. However, it is not clear whether the crystallization occurs in the multilayer. Nevertheless, the lower temperature causes an increase of the viscosity. To study this problem in more detail, the photoreorientation behavior of a series of polymers with different phase transitions will be discussed in a forthcoming paper.

A subsequent irradiation procedure with a changed polarization plane (135°) causes a corresponding reorientation to 45° with respect to the laboratory coordinates. Simultaneously with the induction of optical anisotropy, a significant decrease of the average absorbance is observed. This indicates a decrease of the tilt angle Θ by this process, i.e., a promotion of the homeotropic alignment of the azobenzene side groups.

A further experiment at 56 °C shows that the polarized irradiation of an annealed film results in a comparatively high dichroism. This indicates that an UV irradiation step is not necessarily for an efficient photoorientation process at this temperature, because the molecular aggregation and the tilted orientational order of the primary LB structure are broken thermally.

The high values of optical in-plane anisotropy can be frozen-in by a quick cooling below the glass transition temperature under continued polarized irradiation. As reported, the optical anisotropy is long-term stable in the glassy state. The azimuthal anisotropy is easily erased by heating to 63 °C, but the dichroism can be re-created and modified easily some degrees Centigrade below this temperature compared to the photoreorientation at temperatures below the glass transition.

If the sample is irradiated at 56 °C and the polarized light is switched off, keeping the film at this temperature, the azimuthal orientational direction remains preserved but the dichroism is decreased within 120 min from 0.82 to a stable value of 0.25 (Table 2). The angular-dependent distribution of the in-plane absorbance becomes broader, but the average absorbance is nearly constant during the fading process. This indicates that the tilt angle is only slightly changed. On the one hand, a high anisotropic can be generated temporarily at 56 °C caused by the increased dynamics compared to the room temperature and a sufficient high viscosity in contrast to the liquid-crystalline phase at 63 °C. On the other hand, at 56 °C the high values of dichroism are only stable under the action of polarized light. They decrease dramatically when the ordering force disappears.

After the fading process the sample was cooled down to 20 °C and then irradiated with light of a different polarization direction. The result is a dichroism with a corresponding direction and an amount (0.3) which is typical for films below T_g. Repeated irradiation at 56 °C, however, generates high dichroism values characteristic for this state as described before (Table 3).

Table 4 summarizes the main results depending on film preparation, temperature, and power density. The changes of the average absorbance show that annealing, Vis irradiation, and especially UV/Vis isomerization cycles cause a significant decrease of the in-plane component of the transition moment compared to the initial LB film. In optically isotropic films the procedure results in all cases in a complete photoorientation

Table 4. Photoinduced Order in LB Multilayers and Spin-Coated Film in Dependence on the Preparation and on the Irradiation Conditions[a]

type of film	T (°C)	P (mW/cm^2)	D initial	D end	$A_{end}/A_{initial}$	α (deg)	β (deg)	$\Delta\psi$ (deg)
spin-coated film	20	2	0.02	0.56	0.56	iso	90	
initial LB ML, low ordered	20	2	0.37	0.38	0.75	45	90	45
initial LB ML, high ordered	20	2	0.63	0.59	0.87	45	45	0
initial LB ML, high ordered	20	20	0.63	0.49	0.64	45	75	30
LB ML after UV step	20	2	0.02	0.45	0.59	iso	90	
photoreoriented LB ML	20	2	0.45	0.43	0.54	45	80	35
LB ML after UV step	20	20	0.02	0.65	0.58	iso	90	
annealed LB ML	56	2	0.03	0.81	0.44	iso	90	
LB ML	63	2	0.02	0.01	0.53	iso	iso	0

[a] Dichroism, D, at 330 nm before (initial) and after (end) polarized irradiation. Quotient of average absorbance after polarized irradiation and of the initial film, $A_{end}/A_{initial}$. Angle of the maximum of absorbance before (α) and after (β) linearly polarized irradiation in laboratory coordinates, setting angle γ_P of incident light is always 0°; the reorientation angle is $\Delta\psi = \beta - \alpha$.
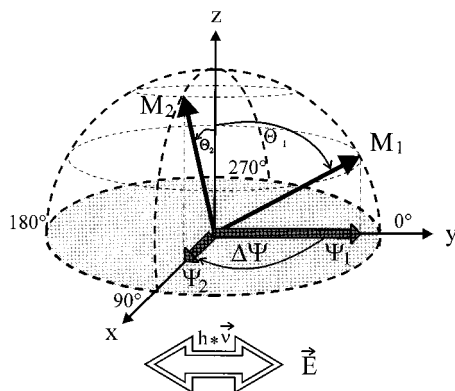
Figure 9. Scheme for the photoreorientation process of an azobenzene moiety from the initial orientation in the *yz*-plane to the *xz*-plane by the reorientational angle $\Delta\Psi$ changing simultaneously the tilt angle Θ. The linearly polarized light of the irradiation procedure is represented by the double arrow with the electric field vector $\vec{E}$ in the *y* direction and the propagation in the *z* direction.

perpendicular with respect to the *E* vector. A high in-plane order in multilayers or in photooriented films restricts the process or results in an incomplete photo-reorientation.

Discussion

The features of photoreorientation within LB multi-layers were studied. The photoreorientation process of azobenzene moieties in the ordered films was compared to the photoorientation in isotropic films of the same liquid-crystalline polymer.

The preparation of multilayers and spin-coated films results in different arrangements of the 2-hydroxyethyl

polyacrylate main chains and the azobenzene side groups. The hydrophilic polyacrylate backbones are layered within the LB film architecture, but they are coiled in the disordered spin-coated films. In the multilayers the azobenzene side groups are arranged in vertical layers tilted toward the dipping direction. This tilt causes an orientational order in the plane and results in azimuthal optical anisotropy. On irradiation with linearly polarized Vis light the azobenzene moieties in spin-coated films become oriented perpendicular with respect to the direction of the electric field vector of the incident light, but in the LB multilayers the strong influence of the homeotropic-like arrangement and the in-plane anisotropy of the tilted azobenzene moieties has to be taken into consideration.

The amphiphilic and thermotropic properties of the model polymer offer the opportunity to prepare films of different supramolecular order, which can be modified by annealing or irradiation. In all films the same photoreaction takes place on the molecular level, but the different states of supramolecular order established by preparation, annealing, or irradiation affect the photo(re)orientation process.

Figure 9 illustrates a scheme for the photoreorientation process in the ordered system. The azobenzene side groups are homeotropically arranged as layers in the *xy* plane and tilted toward the *y* direction. In the model the electric field vector of the linearly polarized light is parallel to the *y* direction. Under the action of the polarized light the moieties become reoriented from the *y* to the *x* direction, where $\Delta\Psi$ is the reorientational angle. Simultaneously, the tilt angle Θ is decreased. This is caused by the homeotropic ordering tendency of the smectic polymer in combination with
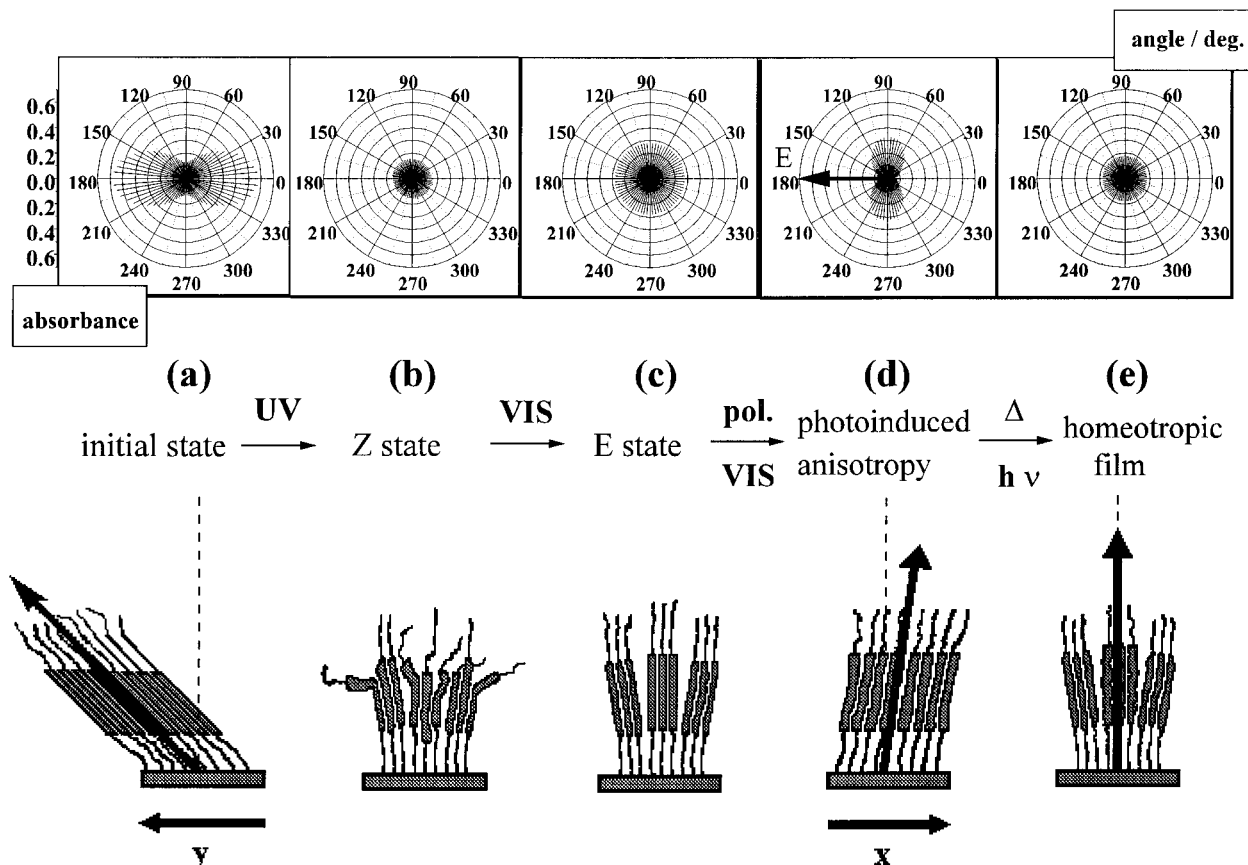

Figure 10. Schematic model for the photoreorientation process in LB multilayer assemblies after photoinduced modification of the in-plane and out-off-plane order. The arrows represent the preferred direction of transition moment of the azobenzene moieties.

the photoorientation to directions perpendicular to the E vector.

The scheme proposed in Figure 10 summarizes the main results concerning the photoreorientation of azobenzene moieties within the LB multilayer assembly of this smectic polymer. In contrast to the photoorientation process in the spin-coated film the linearly polarized Vis irradiation of the virgin, highly ordered LB multilayers does not result in a change of the orientational order. The photoreorientation process is restricted by the dense packing, the strong molecular aggregation, and the orientational order of the azobenzene side groups (Figure 10a), but the photoreorientation takes place after weakening the intermolecular interactions and, in this way, modifying the order and dynamics of the film. This has been achieved by a suitable preparation of the films, annealing of the thermotropic polymer, or UV irradiation. Thus, the stressed, densely packed LB multilayers are modified with rising temperature or by UV irradiation at room temperature. The formation of Z isomers results in deaggregation, the loss of the layered structure, and a decrease of the orientational order down to zero (Figure 10b). In the case of the thermotropic polymer, the UV/Vis irradiation cycle or annealing causes a order−disorder transition from the original LB multilayer to a liquid-crystalline film (Figure 10c).

The photochemically induced disorder or the photochemical "decoupling" of the system can be governed via the wavelength-dependent steady state of the photoisomerization. After such a procedure the photo(re)-orientation process takes place in the less-ordered films, maintaining their layered structure (Figure 10d). The reduction of the in-plane orientational order seems to be the main factor for an efficient photoreorientation process. Such a reorientation process can be repeated many times if the polarization of the incident light is changed with respect to the film. Caused by the linearly polarized light, the azobenzene side groups become reoriented, moving on a cone with its axis normal to the plane of the film.

It has to be pointed out that the opportunity for the modification of optical in-plane anisotropy is governed by the competition of these two principles of ordering−the self-organization of the mesogenic azobenzene side groups which tends to establish a homeotropic alignment and the ordering impact of the linearly polarized light. In this way the photoreorientation process shows a significant temperature dependence on the thermal properties of the liquid-crystalline polymer. Below the glass transition optical anisotropy can only be induced if the restriction of the in-plane orientational order is not too strong. However, once induced it remains stable for months. With increasing temperature, a larger azimuthal dichroism can be photoinduced, while the average absorbance decreases with the progress of the process. This indicates that the tilt angle is decreased (see Figures 9 and 10). Moreover, the photoreorientation process seems to stimulate the homeotropic alignment, because, independent from the polarization, this orientational direction is anyways perpendicular to the electric field vector of the light.

In the smectic mesophase the photoreorientation is restricted by the homeotropic order and the cooperative dynamics of the mesophase (Figure 10e). This indicates that there is an optimum temperature for the induction of a maximum in-plane anisotropy. This temperature depends on the actual order of the respective initial state of the film, the viscosity, and the thermotropic ordering tendency of the polymer. For efficient photo-(re)orientation the initial in-plane and out-of-plane order should be as low as possible. These results are in agreement with our conception concerning the mechanism of photo(re)orientation of azobenzenes in ordered systems.[25−30] In the studied multilayer assembly there are no indications for the photoreorientation mechanism proposed by Palto et al. for ordered systems.[34]

Summarizing, it can be stated that the opportunity of the azobenzene side groups to undergo photoreorientation depends in a sophisticated manner on the order present in the films, the related dynamics, and the exposure conditions concerning wavelength, polarization direction, intensity, and exposure time. The photoinduced reorientation process in the multilayer of the thermotropic polymer is controlled by the molecular aggregation of the azobenzene moieties, the primary in-plane and out-of plane order, the ordering tendency of the liquid-crystalline polymer, and the temperature. In a forthcoming paper the photoorientation of a spin-coated film and the connection of this process with the molecular aggregation and ordering phenomena of the polymer will be presented as a function of temperature and irradiation conditions.

References and Notes

(1) Penner, T.; Schildkraut, J. S.; Ringsdorf, H.; Schuster, A. *Macromolecules* **1991**, *24*, 1041.
(2) Geue, Th.; Stumpe, J. Möbius, G.; Pietsch, U.; Schuster, A.; Ringsdorf, H. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 405.
(3) Geue, Th.; Stumpe, J.; Pietsch, U.; Haak, M.; Kaupp, G. *Mol. Cryst. Liq. Cryst.* **1995**, *262*, 157.
(4) Möbius, G.; Pietsch, U.; Geue, Th.; Stumpe, J.; Schuster, A.; Ringsdorf, H. *Thin Solid Films* **1994**, *247*, 235.
(5) Geue, Th.; Stumpe, J.; Möbius, G.; Pietsch, U.; Schuster, A.; Ringsdorf, H.; Kaupp, G. *J. Inf. Rec. Mater.* **1994**, *21*, 645.
(6) Stumpe, J.; Geue, Th.; Fischer, Th.; Menzel, H. *J. Inf. Rec. Mater.* **1996**, *23*, 107.
(7) Ziegler, A.; Geue, Th.; Stumpe, J. *J. Inf. Rec. Mater.* **1996**, *23*, 111.
(8) Geue, Th.; Pietsch, U.; Stumpe, J. *Thin Solid Films* **1996**, *284−285*, 228.
(9) Stumpe, J.; Geue, Th.; Fischer, Th.; Menzel, H. *Thin Solid Films* **1996**, *284−285*, 606.
(10) Menzel, H.; Weichart, B.; Schmidt, A.; Knoll, W.; Stumpe, J.; Fischer, Th. *Langmuir* **1994**, *10*, 1926.
(11) Menzel, H.; Weichart, B.; Hallensleben, L. *Polym. Bull.* **1992**, *27*, 637.
(12) Menzel, H.; Hallensleben, L.; Weichart, B.; Schmidt, A.; Knoll, W.; Fischer, Th.; Stumpe, J. *Macromolecules* **1993**, *26*, 3644.
(13) Stumpe, J.; Fischer, Th.; Menzel, H. *Macromolecules* **1996**, *29*, 2831.
(14) Kawanishi, Y.; Kamaki, T.; Seki, T.; Sakuragi, M.; Ichimura, K. *Mol. Cryst. Liq. Cryst.* **1992**, *218*, 153.
(15) Sawodny, M.; Schmidt, A.; Urban, C.; Ringsdorf, H.; Knoll, W. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 217.
(16) Sawodny, M.; Schmidt, A.; Stamm, M.; Knoll, W.; Urban, C.; Ringsdorf, H. *Thin Solid Films* **1992**, *210/211*, 500.
(17) Sawodny, M.; Schmidt, A.; Stamm, M.; Knoll, W.; Urban, C.; Ringsdorf, H. *Polym. Adv. Technol.* **1991**, *2*, 127.
(18) Todorov, T.; Nikolova, L.; Tomora, N. *Appl. Opt.* **1984**, *23*, 4309.
(19) Barnik, M. I.; Kozenkov, V. M.; Shtykov, N. M.; Palto, S. P.; Yudin, S. G. *J. Mol. Electron* **1989**, *5*, 53.
(20) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid. Commun.* **1987**, *8*, 59. Eich, M.; Wendorff, J. H. *Makromol. Chem., Rapid. Commun.* **1987**, *8*, 467.

(21) Xie, S.; Nathansohn, A.; Rochon, P. *Macromolecules* **1992**, *25*, 2268, 5531.

(22) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*; VCH Publishers: New York, 1995.

(23) Blinov, L. M. *J. Nonlinear Opt. Phys. Mater.* **1996**, *5*, 165.

(24) Shibaev, V. P. *Polymers as Elektrooptical and Photooptical Media*; Springer: New York, 1996.

(25) Fischer, Th.; Läsker, L.; Stumpe, J.; Kostromin, S. *J. Photochem. Photobiol., A* **1994**, *80*, 4531.

(26) Läsker, L.; Fischer, Th.; Stumpe, J.; Kostromin, S.; Ivanov, S.; Shibaev, V.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 347.

(27) Stumpe, J.; Läsker, L.; Fischer, Th.; Kostromin, S.; Shibaev, V.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1994**, *253*, 293.

(28) Stumpe, J.; Läsker, L.; Fischer, Th.; Geue, Th. *J. Inf. Rec. Mater.* **1994**, *21*, 449.

(29) Stumpe, J.; Läsker, L.; Fischer, Th.; Rutlow, M.; Kostromin, S.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1994**, *261*, 371.

(30) Stumpe, J.; Läsker, L.; Fischer, Th.; Rutlow, M.; Kostromin, S.; Ruhmann, R. *Thin Solid Films* **1996**, *284−285*, 252.

(31) Ichimura, K.; Hayashi, Y.; Kawanishi, Y.; Seki, T.; Tamaki, T.; Ishizuki, N. *Langmuir* **1993**, *9*, 857.

(32) Janossy, I. *Phys. Rev. E* **1994**, *49*, (4), 2957.

(33) Pararo, D.; Maddalena P.; Abbate, G.; Santamato, E.; Janossy, I. *Mol. Cryst. Liq. Cryst.* **1994**, *251*, 73.

(34) Palto, S. P.; Durand, G. *J. Phys. II France* **1995**, *5*, 963.

(35) Blinov, L. M.; Barnik, M. I.; Mazzula, A.; Umeton, C. *Mol. Mater.* **1995**, *5*, 237.

(36) Barnik, M. I.; Zolot'ko, A. S.; Rumyantsev, V. G.; Terskov, D. B. *Crystallogr. Rep.* **1995**, *40*, 746.

(37) Palto, S. P.; Shtykov, N. M.; Khavrichev, V. A.; Yudin, S. G. *Mol. Mater.* **1992**, *1*, 3.

(38) Palto, S. P.; Malthete, J.; Germain, C.; Durand, G. *Thin Solid Films* **1997**, in press.

(39) Schönhoff, M.; Mertesdorf, M.; Lösche, M. *J. Phys. Chem.* **1996**, *100*, 7558.

(40) Schönhoff, M.; Chi, L. F.; Fuchs, H.; Lösche, M. *Langmuir* **1995**, *11*, 163−168.

(41) Kasha, M. *Radiat. Res.* **1963**, *20*, 55−71.