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PHOTOORIENTATION IN LB MULTILAYERS OF THERMOTROPIC POLYMERS

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Abstract The photoreorientation of azobenzene side groups is studied in LB multilayers of different order and compared to the process in spin–coated films of the same smectic polyacrylate and "hairy rod" polyglutamates. The photochemically induced reorientation process depends on the aggregation of the azobenzene moieties, the supramolecular order of the films, the enthalpic stability of the mesophase in the case of the LB multilayers of thermotropic polyglutamates and on the irradiation conditions. The stable nematic–like order of the "hairy rod" polyglutamate backbones influences the photoreorientation of the azobenzene side groups in the LB films. In all cases the photoreorientation process becomes more efficient after weakening the intermolecular interactions by a suitable preparation of the films, on irradiation in the viscous–elastic state or by a temporary photochemical decoupling of the supramolecular order.

INTRODUCTION

The manipulation of the supramolecular structure of LB multilayers is of great interest. In the case of thermotropic polymers with photochromic azobenzene side groups a modification of the vertical and the in–plane order may be achieved by annealing[1,2] or by irradition[3–6]. In both cases the intermolecular interactions of the stressed LB multilayers are weakened by raising temperature or by establishing a steady state of the photoisomerization. Such procedures result in modified structures caused by the thermotropic self–organization of the polymers[1–6].

In addition to the well–known effect of photochromism the E–Z photoisomerization causes a change of the geometrical shape, the polarity and the direction of the transition moment of the azobenzene moiety. In this way the molecular photoreaction modifies the intermolecular interactions and thus the supramolecular structure of the multilayer.

The interaction of photochromic moieties with linearly polarized light offers a new way to align them[7–13]. In this way optical anisotropy is generated or modified in polymer films. The photoorientation process takes place via a number of angular–dependent

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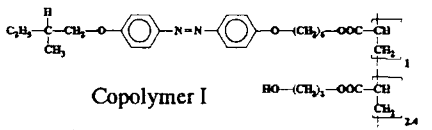
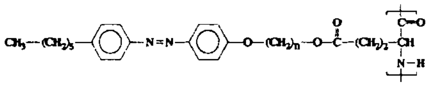
photoselection events, photoisomerization cycles and directed rotational diffusion in the steady state of the photoreaction[10]. It results in the (re)orientation of the photochromic groups perpendicular to the direction of the electric field vector of the incident light. The aim of the study is to compare the photoorientation process of the azobenzene moiety in LB multilayers of different order in comparison to that in the spin-coated films of the same smectic polyacrylate and "hairy rod" polyglutamates.

LB MULTILAYERS

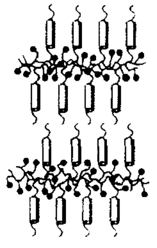
Polymers like 2-hydroxyethyl polyacrylate[1] I and polyglutamates[2] II with photochromic azobenzene side groups combine amphiphilic and thermotropic properties. In contrast to polyacrylates with flexible backbones polyglutamates represent polymers of the "hairy rod" type, which are characterized by a stiff rod-like polypeptide helix. Rod-like azobenzene side groups are attached via flexible alkyl spacers to the backbone. The preparation of LB multilayers and spin-coated films results in different arrangements of the main chains and the azobenzene side groups within the films. Thus, the optical properties of the layered LB films of both systems are governed by the preferred orientation of the azobenzene side groups which show a tilt in the dipping direction causing optical in-plane anisotropy, whereas the spin-coated films are optically isotropic. The hydrophilic polyacrylate backbones are layered within the LB film, but they are coiled in the disordered spin-coated film. A nematic-like arrangement of the polypeptide rods with a preferred orientation along the dipping direction is established in the LB layers of the polyglutamates, whereas the side groups are tilted with respect to the helical backbone[2].



Copolymer I

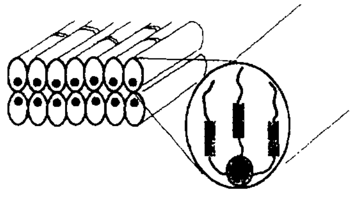


Polymer II



← Lamellar LB Structure of I
g 30 k 56 s 86 i

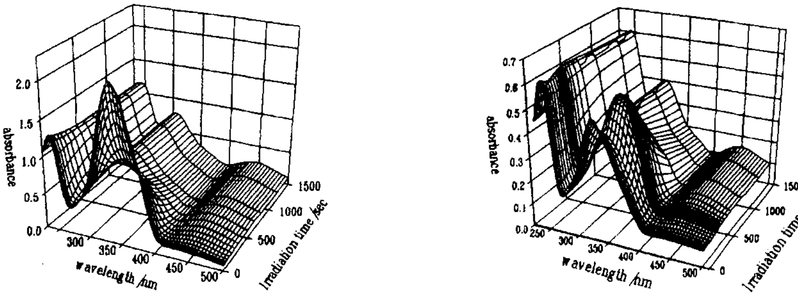
Layered LB structure of
"Hairy rod" polymers II →
n=2 g 35 lc 181 ch
4 g 37 lc_1 81 lc_2 178 ch
6 52 lc_2 163 ch



RESULTS

In both LB systems the initial double layered structures are irreversibly destroyed upon UV irradiation (365nm) and the azimuthal anisotropy of the azobenzene absorbance is lost. Compared to the behavior in solution and in spin-coated films, the irradiation of the LB multilayers shows a different decrease of absorbance because the photoisomerization is connected with a photochemically stimulated deaggregation process and a modification of the orientational order[6] (Figure 1b).

Subsequent VIS irradiation (457 nm) generates less ordered lamellar structures with modified spacing which are very similar to those of the polymers in the bulk. In the case of the smectic polyacrylate **I** the procedure results in optically isotropic films of homeotropically aligned azobenzene moieties[3]. In LB films of the "hairy rod" polyglutamates **II** the orientation of the side groups in relation to the stable main chain helices is modified differently by the UV/VIS irradiation cycle depending on the length of the alkylene spacer between the backbone and the photochromic moiety. An increased length results in a higher liquid crystalline ordering tendency of the polymers. Thus, in the case of a hexamethylene spacer an arrangement of the chromophores parallel to the main chain helices is restored causing optical anisotropy in the films. The short ethylene spacer, however, results in an isotropic distribution of the chromophores[6].



a) b)

FIGURE 1 UV/VIS spectra of a Polymer II/4 as spin-coated film (a) and as a multilayer (b) in dependence on the irradiation time (λ_{ex}= 365 nm)

Upon irradiation of spin-coated films of both polymers using linearly polarized Vis light (457 nm) optical anisotropy is induced in the initially isotropic films. The azobenzene moieties become oriented perpendicular with respect to the electric field vector of incident light.

LB multilayer of the polyacrylate

However, in the case of a highly ordered LB multilayer in its virgin state, the identic irradiation (P= 2mW/cm^2) procedure does not result in a change of the primary orientational order of the side groups. The photoreorientation is suppressed by their dense packing, the orientational ordOer and the strong molecular aggregation of the azobenzene side groups. However, the process takes place using a higher power density (P= 20mW/cm^2, Fig. 2). But the maximum of azimuthal dichroism is only shifted to 75° with respect to the E vector. Irradiating with P= 2mW/cm^2 the process can be detected also in less ordered multilayers prepared with lower surface pressure (Table 1). However, after an initial UV exposure the irradiation with linearly polarized VIS light induces a new orientational order of the azobenzene side groups to a much higher extend in the case of the initially highly ordered LB films (Figure 3). The decrease of absorbance indicates that the tilt angle becomes smaller. Thus, the photoorientation process stimulates a more perfect homeotropic alignment of the side groups.

The VIS irradiation is always connected with the formation of a new layered structure. The photoorientation process takes place also after an intermediate non-polarized UV/VIS irradiation cycle or after annealing in the viscous-elastic state. For the photoinduced reorientation process the initial double layered structure and the molecular aggregation of the azobenzene moieties have to be destroyed. The comparison of the process at different temperatures shows that a much stronger azimuthal dichroism is photoinduced in the viscous-elastic state of the polymer at 63 °C (spectroscopic degree of order S=0.72) than at room temperature (S=0.20).

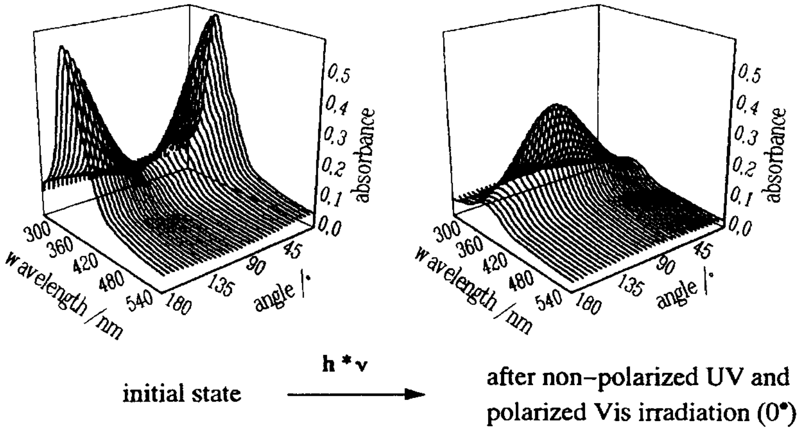


FIGURE 2 Angular-dependent UV/VIS spectra of the initial LB Multilayer of I before and after polarized irradiation (457nm, 20mW/cm^2, electric field vector at 0°).

The high value of optical anisotropy induced in the mesophase can be frozen-in by cooling down immediately after switching off the laser. However, the photoinduced anisotropy relaxes to a value of 0.2 if the temperature is kept at 63°C after the irradiation.

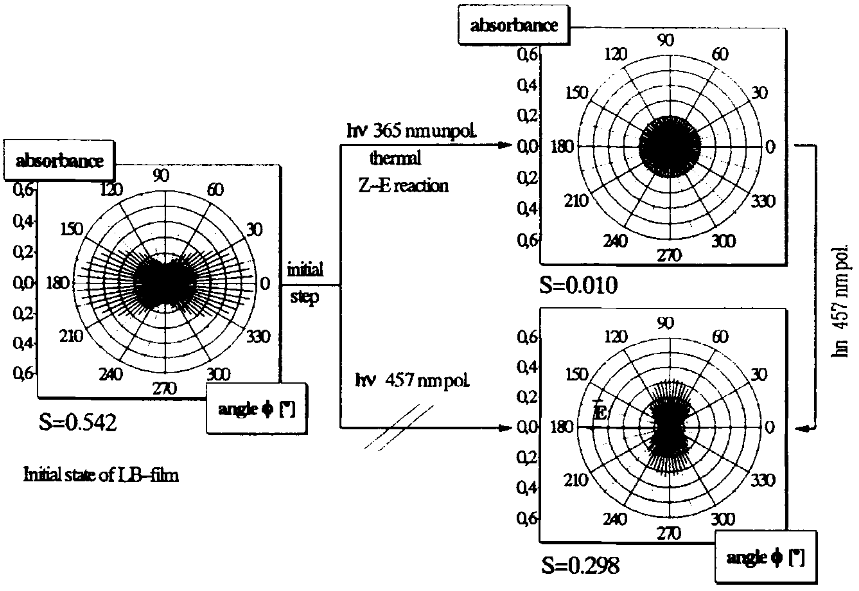


FIGURE 3 Polar diagramm of absorbance at 340 nm of a LB multilayer of I before, after UV irradiation (365nm) and subsequent irradiation with linearly polarized light (436nm, 2mW/cm^2, electric field vector E at 0°).

Compared to the LB multilayer the dichroism induced at room temperature in the spin–coated film is much higher (S=0.32). The difference seems to be caused by the tilted arrangement of the azobenzene side groups in the vertically layered structure of the LB film. The irradiation with polarized VIS light of changed polarization direction causes the corresponding azimuthal reorientation in both types of films. In this way the optical in-plane anisotropy can be modified several times.

TABLE 1 Photoinduced order in LB multilayers and spin–coated films of Polymer I dependent on preparation and irradiation conditions.

Films and Multilayers	P mW/cm²	S_{sp}(start)	S_{sp}(end)	$\Delta\Psi_{set}$	$\Delta\Psi_{actual}$
new spin–coated film	2	0	0.32	-	-
spin–coated film	2	0.32	0.28	45	45
new spin–coated film after UV irr.	2	0	0.35	-	-
initial LB-ML	2	0.16	0.20	45	45
initial LB-ML	2	0.54	0.53	45	0
initial LB-ML	20	0.54	0.37	90	75
LB-ML after UV irradiation	2	0	0.30	45	45
LB-ML	2	0.30	0.28	45	35
LB-ML after UV irradiation	20	0	0.53	45	45
LB-ML in viscous–elastic state	2	0	0.72	45	45

$\Delta\Psi_{set}$ theoretical expected angle for the complete photoreorientation
$\Delta\Psi_{actual}$ angle between the director before and after irradiation

LB multilayer of polyglutamates

In contrast to the behavior in spin–coated films, the photoinduced reorientation process is restricted in the original LB multilayers of polyglutamates **II**. This seems to be caused by the high orientational order and by H–aggregation of the azobenzene moieties. But efficient photoorientation takes place in some multilayers after weakening the intermolecular interactions and decreasing the order by an initial UV exposure[6]. After an UV/VIS irradiation cycle the degree of order is small in the case of a polyglutamate with the short ethylene spacer and the azobenzene side groups can be photoreoriented to any desired azimuthal angle in relation to the aligned main chain rods changing the direction of electic field vector of the incident light with respect to the multilayer. The photoinduced dichroism decreases with increasing angle between the aligned main chain helices and the preferred direction of the azobenzene moieties up to 90°. It shows a minimum for a photoinduced orientational order perpendicular to the backbone.

However, the photoinduced reorientation process is restricted almost completely in the LB multilayer of the polymer with the hexamethylene spacer. This polyglutamate is characterized by a much higher transition enthalpy of its mesophases. A longer spacer causes a stronger decoupling of the side group from the backbone, but simultaneously it strengthens the liquid crystalline order. Even if the initial order is destroyed by UV irradiation, the VIS light immediately reconstructs the orientational order of the side groups in the direction of the main chain helices. In this case the permanent nematic-like layered arrangement of the "hairy rod" backbones acts as an aligning force for the temporary photochemically decoupled side groups.

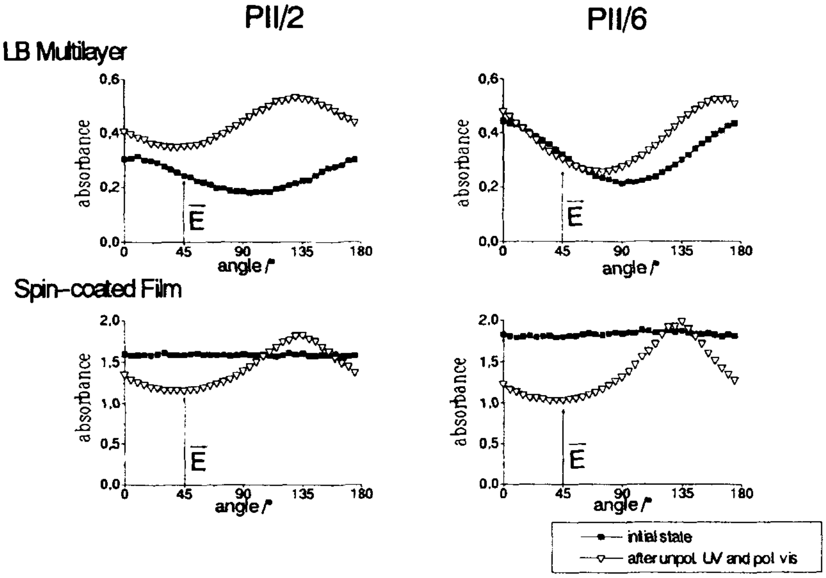


FIGURE 4 Comparison of polarized absorbance at 348nm before and after irradiation of LB and spin-coated films of PII/6 and PII/2, E indicates the electric field vector.

TABLE 2 Polarized irradiation of spin-coated films and LB multilayer of polyglutamates **II**. Preferred orientation and degree of order.

	Spin-coated Film		LB Multilayer			
Polymer	S_{sp} (start)	S_{sp} (end)	S_{sp} (start)	S_{sp} (end)	$\Delta\Psi_{real}$	$\Delta\Psi_{norm}$
Polarized Vis irradiation						
II/2	0	0.114	0.265	0.18	25°	45°
II/4	0	0.115	0.26	0.255	15°	45°
II/6	0	0.13	0.31	0.27	5°	45°
Non-polarized UV irradiation and subsequent polarized Vis irradiation						
II/2	0	0.168	0.26	0.16	45°	45°
II/4	0	0.115	0.4	0.285	40°	45°
II/6	0	0.23	0.3	0.26	20°	45°

ΔΨ angle between the preferred orientational direction before and after irradiation

Thus, the strength of the interactions between the rod-like polypeptide helices and the photochromic moieties depends significantly on the spacer length controlling the mobility of the side groups and the enthalpic stability of the liquid crystalline order. In the case of high enthalpic stability the preferred orientational direction of the side groups governed by the aligned helices is only slightly changed by the photoreorientation process. Thus, the efficiency of the photoreorientation process decreases with increasing lenght of the spacer (n=2>4>6). This is caused by the increasing tendency to establish the liquid crystalline order in this serie of polymers with prolonged spacer between the two different mesogenic moieties. Contrary, in the spin-coated films the photoinduced optical anisotropy is higher for the polymers with longer, more flexible spacer (Fig. 4).

CONCLUSION

Comparing the influence of light on the LB systems and the spin-coated films, the same photoreaction takes place on molecular level, but a different supramolecular order is established in the films. On non-polarized exposure and on irradiation with linearly polarized light the photoinduced supramolecular structure depends on the initial order and the ordering tendency of the polymers. The comparison of the photoreorientation process in the two LB systems demonstrates the influence of the different backbones within the layered structures of both types of thermotropic polymers. While in the case of the polyacrylate **I** the azimuthal orientational order of the homeotropically aligned azobenzene side groups can be reoriented easily by linearly polarized light, the permanently aligned polypeptide helices of **II** cause a command effect on the photochromic, rod-like side groups of the combined liquid crystalline main and side chain polymers. Regardless of the photoinduced disorder of the side groups the stable nematic-like in-plane order of the "hairy rod" helices influences the ability to undergo photoreorientation. In addition the process depends on the angle between the directions of the two aligning forces, i.e. the photoorientation process and the thermotropic self-organization. The first one is controlled by the electric field vector of the incident light, and the second one by the direction of the aligned polypeptide backbones.

A strong initial order may restrict the ordering impact of the linearly polarized light. In aligned films a competition between two principles of order – the self-organization of mesogenic side groups and the photoorientation process – takes place. Thus, the initial order within the photochromic films should be as low as possible for an efficient photoorientation process. This has been achieved by a suitable preparation of the films or by a "temporary photochemical decoupling" of the supramolecular order in a steady state of the photoreaction weakening the intermolecular interactions. The E–Z photoisomerization causes a decrease of the orientational order, breaking the aggregation and inducing higher mobility.

In the LB multilayers of thermotropic polymers the photoorientation process of the same photochromic moiety is controlled by molecular aggregation, actual order of the system, ordering tendency of liquid crystalline polymers, the wavelength of incident light and by the temperature.

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