Langmuir−Blodgett Films of Photochromic Polyglutamates. 9. Relation between Photochemical Modification and Thermotropic Properties

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ABSTRACT: Thermotropic polyglutamates with photochromic azobenzene side groups are polymers of the "hairy rod" type. They form LB multilayer assemblies, in which the rod-like macromolecules are oriented in the dipping direction. The initial LB films have a well-defined bilayer structure in which the rod-like azobenzene moieties are tilted toward the α-helical backbones and form H-aggregates. The change of aggregation and orientational order of the azobenzene chromophores is studied for polyglutamates with different spacer lengths upon irradiation and annealing. The lamellar order and in-plane anisotropy of the chromophores is irreversibly lost on UV irradiation. New ordered structures with a more symmetric distribution of the side chains around the main chain helix, a modified spacing, changed aggregation, and a different in-plane anisotropy are established after subsequent vis irradiation or annealing. The established supramolecular order strongly depends on the spacer length. A shorter spacer (C_2) between the backbone and the photochromic moiety causes an isotropic in-plane distribution of the chromophores, whereas in the case of longer spacers (C_4 or C_6) an arrangement of the chromophores parallel to the main chain helices is restored. The change in the molecular arrangement of the side groups is controlled by the ordering tendencies and the dynamic properties of the combined liquid crystalline main and side chain polymers.

Introduction

Photoreceptors in biological systems are supramolecular assemblies of polypeptides with photochromic moieties. Their mechanism is based on conformational changes of the macromolecules due to the photochemically induced modification of the interaction between the photochromic moiety and the macromolecule upon exposure with light.[1] Similar concepts of operation have been studied in material science[2−6] in the last years. In addition to the well-known molecular photoreactions which change the molecular structure, in the case of ordered systems like liquid crystalline polymers or LB multilayers, a variation of the optical properties can be induced by photochemical modification of the supramolecular order.[5−18] Such changes can be realized by photochemically induced, permanent or temporary variation of weak intermolecular interactions, which determine the supramolecular order. Under this aspect the photochemical induction or modification of order[7−9] and the photostimulated change of the orientational direction[9−18] have been studied as new approaches for optical data storage, optical components, or full optical devices. The mutual interaction of molecular photoreactions and supramolecular order is currently under investigation.

The α-helical structure of polypeptides stabilized by hydrogen bonds give the macromolecules a rigid rod-like shape. The attachment of long flexible alkylene side chains results in thermotropic polypeptides,[19−24] in which the α-helical backbones act as mesogenes. Such polypeptides are polymers of the "hairy rod" type,[24−28] forming layered, cholesteric, or columnar ordered structures. Liquid crystallinity can also be realized by attaching stiff rod-like side groups to the backbone via flexible spacers, as shown in Figure 1. Thus, smectic and cholesteric mesophases were observed in the case of a polyglutamate with alkoxybiphenyl moieties.[31]

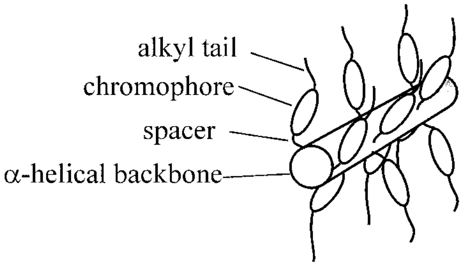

Figure 1. Schematic representation of a polyglutamate with a stiff α-helical backbone and mesogenic azobenzenes in the side chains connected by flexible spacers.

Polypeptides of the hairy rod type form densely packed monolayers with a two-dimensional nematic arrangement of the rod-like macromolecules, when they spread at the air−water interface.[29] This arrangement is oriented macroscopically by the shear forces present in the LB transfer process.[30] They can be deposited on substrates by the LB technique.[31−33] In this way anisotropic LB multilayers are formed, in which the rigid main chain helices are preferentially oriented toward the dipping direction.[30] The domain structure of a conventional monolayer is broken up due to the orientation of the polypeptide rods and the flexibility of the side groups. By this reason LB films of hairy rod polymers are very homogeneous, are nearly free of defects,[34] and have excellent optical properties.[35]

The concept of hairy rod polymers has been extended to polymers with mesogenic side groups attached to the polymer backbone via flexible spacers.[24,31] The studied thermotropic polyglutamates combine the ability to form monolayers at the air−water interface with the ability of thermotropic self-organization.[42] Thus, liquid crystalline ordered states are established in the bulk at certain temperatures. Therefore, these polymers can

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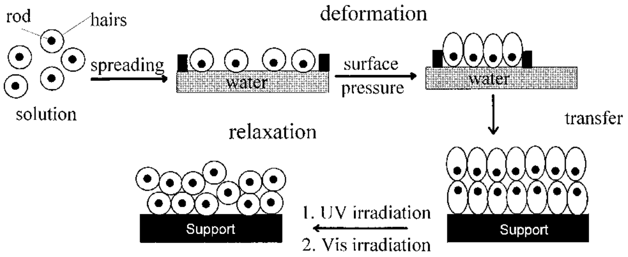


Figure 2. Scheme for deformation and orientation of the hairy rods at the air−water interface and relaxation within the LB film.

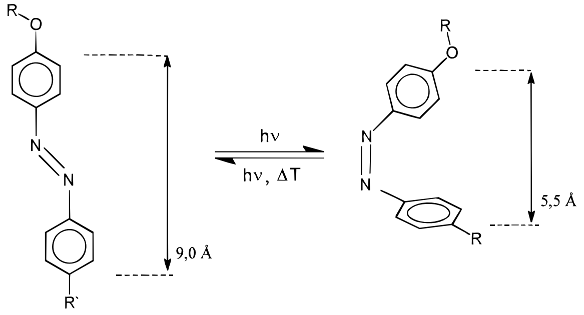


Figure 3. Photoisomerization of azobenzene derivatives.

form supramolecular assemblies either by their amphiphilic properties or by their thermotropic properties. The functionalization with azobenzene moieties as mesogenic side groups offers the opportunity to manipulate the initial LB structure by irradiation or thermal treatment.

As determined by X-ray measurement,[33,36,37] the initial multilayer assemblies of the studied azobenzene-substituted polyglutamates exhibit a bilayer structure of deformed hairy rods. The asymmetric deformation of the hairy rod is caused by the interaction with the polar air−water interface and the applied surface pressure[38] (see Figure 2). While the deformation is lost in the case of hairy rod polymers with alkyene side chains,[39−41] it is retained in the case of the polyglutamates with rod-like side groups due to the stronger lateral interactions.[33,38] Both the induced deformation and the transfer process cause an azimuthal arrangement of the side groups toward the dipping direction, which results in optical in-plane anisotropy.[33]

Upon irradiation the azobenzene moieties undergo $E-Z$ photoisomerization and a wavelength-dependent steady state between the rod-like E isomer and the more globular Z isomer is established (Figure 3). The Z isomer has a different electronic structure, geometrical shape, and polarity, as well as changed extent and direction of the transition moment. However, the Z isomers are thermodynamically unstable and undergo a thermal $Z-E$ isomerization to the stable E isomers.

The changes of the molecular properties of the photochromic group due to photoisomerization cause a modification of the intermolecular interactions of the ordered systems and result in a change of the supramolecular order. Thus, in solution the photoisomerization can induce a helix to coil transition of photochromic polypeptides.[43,44] In aligned films of liquid crystalline polymers the photochemical switch-off of the azobenzene mesogenicity decreases the initial order.[9] On subsequent vis irradiation the degree of order of these films is quite differently, modified for polymer with different spacer lengths. A relation between the liquid crystalline properties of the polymers, especially the enthalpic stability of the mesophase, and the photochemically established order is suggested.[9,18,45]

Table 1. Characteristic Data for the Polymers[a]

	P2	P4	P6
spacer	ethyl	butyl	hexyl
molecular weight (GPC)[b]	35 000	12 500	70 000
λ_{max} ($CHCl_3$) (nm)	348	350	350
area per monomeric unit "initial" (nm^2)	0.27	0.32	0.33
area per monomeric unit "Z" (nm^2)	0.41	0.51	0.57
area per monomeric unit "E" (nm^2)	0.27	0.34	0.33
collapse pressure "initial" (N/m)	50×10^{-3}	53×10^{-3}	50×10^{-3}
collapse pressure "Z" (N/m)	21×10^{-3}	18×10^{-3}	33×10^{-3}
collapse pressure "E" (N/m)	50×10^{-3}	31×10^{-3}	37×10^{-3}
max surface pressure for transfer (N/m)	35×10^{-3}	40×10^{-3}	25×10^{-3}

[a] For explanation of the designations "initial", "Z", and "E" see text. [b] Estimated from GPC calibrated with polystyrene standards.

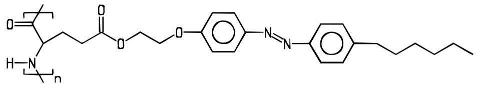
Recently, we have shown that the layered structure of LB multilayer assemblies of amphotropic 2-hydroxyethyl polyacrylates with azobenzene moieties as side groups is reversibly modified upon irradiation.[15−17] A similar behavior was found for LB films of the "hairy rod" polyglutamates with azobenzene side groups. On irradiation the asymmetric bilayered structure is lost[33] (see Figure 2), and after a UV/vis irradiation cycle and the concomitant relaxation of the hairy rod polymer, a new arrangement of the side groups is established.[31−33] The orientational order of the main chain helices remains unchanged after all procedures, as has been confirmed by polarized FT-IR spectroscopy.[31]

To our knowledge there is not any information about the interaction of the two different mesogenic moieties and its thermally and/or photochemically induced variation in LB films of the hairy rod polymers, which represent layered and aligned films of combined liquid crystalline main and side chain polymers. The aim of this contribution is to study the change of the molecular aggregation and the orientational order of the azobenzene side groups in LB multilayers of these thermotropic polyglutamates upon irradiation and/or annealing with dependence on the length of the alkyl spacer.

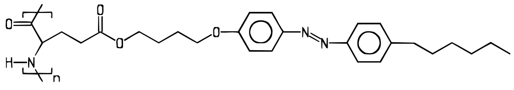
Experimental Section

Materials. The investigations were carried out with poly(2-(4-((4-hexylphenyl)azo)phenoxy)ethyl L-glutamate) (P2), poly(4-(4-((4-hexylphenyl)azo)phenoxy)butyl L-glutamate) (P4), and poly(6-(4-((4-hexylphenyl)azo)phenoxy)hexyl L-glutamate) (P6). The synthesis, characterization and spreading behavior of these materials was described earlier.[31] The characteristic data are compiled in Table 1.

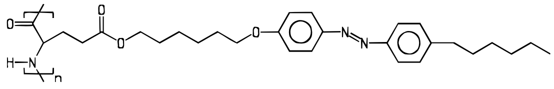
P2



P4



P6



Quartz slides (Hellma, Suprasil fused silica optical windows; UV/vis spectroscopy) and silicon wafers (Wacker Chemie, FT-IR spectroscopy) were used as substrates for the LB films. After rinsing with chloroform, the cleaning process included successive treatment with surfactants, 25% ammonia/30% H_2O_2 (1:1) and nitric acid, in an ultrasonic bath. The substrates cleaned in this way were hydrophilic and were subsequently made hydrophobic by exposure to hexamethyldisilazane vapor for 12 h.

Instruments and Methods. The polymers were spread from chloroform solutions on a Lauda FW 1 trough filled with ultrapure water (>18 MΩ cm, Barnsteadt NanoPure III). After a period of at least 15 min the film was compressed to the intended surface pressure. After the surface area had stabilized at this pressure, the transfer was started using a Lauda FL-1E film lift. The dipping rate was adjusted to 25 mm/min. The transfer ratios were determined from the decrease in the surface area.

DSC experiments were carried out using a Perkin-Elmer DSC7 instrument. The heating and cooling rate was 10 K/min. The X-ray diagrams of fibers were obtained using a flat film camera and Cu Kα radiation.

Irradiations were carried out using a 250 W XBO (Narva), employing metal interference filters to obtain light with wavelengths of 365 and 436 nm, respectively. A cuvette filled with water was used to remove the IR radiation. The light was directed perpendicular to the surface of the LB film.

An LB film is called "initial" when a dark-adapted solution is spread to a monolayer and this monolayer is transferred to an LB film under red light conditions to ensure that all azobenzene moieties are *E* isomers. It is called "*Z*" when an "initial" film is irradiated with UV light ($\lambda_{\max} = 365 \pm 5$ nm) until the photostationary state is reached (about 10 min). LB films called "*E*" are obtained by irradiating "*Z*" films with visible light ($\lambda = 436 \pm 5$ nm) until the photostationary state is reached (about 5 min).

The supermolecular structures of LB multilayer assemblies were characterized by UV/vis spectroscopy, X-ray measurements,[33,36,37] and the Ehringhaus compensation method. The complex states of the azobenzene moieties are analyzed concerning their aggregation, orientation, and the ratio between *Z* and *E* isomers. The orientational order was studied using polarized UV−vis spectroscopy, because the transition moment of the *E* azobenzene moiety is directed along the long axis of the molecule. The absorbance, the shape of the band, and the wavelength of maxima or shoulders give information about the aggregation and the orientation.

Polarized UV/vis spectra were recorded on a Perkin-Elmer Lambda 19 instrument, equipped with a set of Glan-Taylor prism polarizers made of calcite (LOT). The spectroscopic degrees of order were calculated by

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}$$

$A_{\parallel}$ = absorption at the preferred direction

$A_{\perp}$ = absorption perpendicular to this direction

The aggregation of the chromophores was investigated using a semiquantitative fitting procedure for the $\pi-\pi^*$ band in the UV/vis spectra, which was described in detail recently.[33] The starting point for this procedure was the spectrum of a low molecular weight model (2-(4-((4-(hexyloxy)phenyl)azo)phenoxy)ethyl acetate) in chloroform. The peaks were classified with different aggregates according to the scheme of Kunitake.[46,47] The amounts of the different aggregates were determined as the area of the corresponding peak.

Results

Thermotropic Bulk Properties. The thermotropic bulk properties of the azobenzene-substituted polyglutamates P2, P4, and P6 were studied by means of DSC, polarizing microscopy, and X-ray measurements. The temperatures and the corresponding enthalpies of the mesophase transitions are summarized in Table 2.

Two endothermic transitions were found for the polymers, the first more complex transition between 33 and 81°C and a second one in the range of 164−183 °C. Upon cooling or on second heating, only the higher transition can be detected. After annealing, the first transitions can be reproduced too, but they have been shifted to lower temperatures. This transition is more pronounced in the polymers with the shorter spacer. In agreement with other studies[36,48,49] the first step seems to be related to a glass transition caused by the side chains. In agreement with several other side chain polymers[9] T_g should be decreased due to the increasing spacer length; a T_g for P6 was not detected but it should be lower than those of P2 and P4. It looks like P4 and P6 exhibit very weak phase transitions in this temperature range.

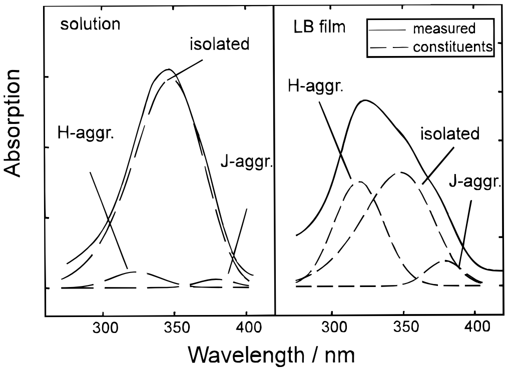


Figure 4. Example for the peak-fitting procedure. Peak fitting of the spectra of P2 in solution and as an LB film (80 layers), the $\pi-\pi^*$ band of the model is the peak designed isolated in the spectrum of the solution. For detailed information see the text and ref 33.

Table 2. Temperatures and Enthalpies of Phase Transitions for P2, P4, and P6[42] after (a) First Heating and (b) Second Heating and (c) after Annealing

			1. peak		2. peak	
polymer	state	T_g/°C	T/°C	ΔH/kJ mol^{-1}	T/°C	ΔH/kJ mol^{-1}
P2	a	36			180	2.67
	b				184	1.84
	c	33			178	1.62
P4	a			1.17	183	6.17a
	b				184	4.23a
	c	37	81	0.19	178	2.13a
P6	a		58	0.48	164	6.56
	b				163	6.51
	c		52	0.09	161	6.29

The thermotropic properties of polymers P2, P4, and P6 resemble those of a polyglutamate with hexoxybiphenyl moieties and a butyl spacer, for which two transitions at 143 and 222 °C have been detected.[20] The comparison with the results of Watanabe[20] indicates that the photochromic polyglutamates form two ordered states which can be assigned to a smectic-like layered structure and a less ordered cholesteric phase at temperatures above 160−180 °C. As shown in Table 2, the temperatures and enthalpies of the high-temperature transitions are influenced by the length of the spacer. The polymer with the hexamethylene spacer shows the sharpest transition and the highest enthalpy. The transition enthalpies in the second heating cycle clearly demonstrate the higher ordering tendency of the polymers with increasing number of methylene units in the alkyl spacer. The thermotropic properties of the photochromic polyglutamates, especially the nature of the low-temperature transition are still under investigation and will be the subject of a forthcoming publication.[36]

Table 3. Spacings *d* Determined by X-ray Measurements in Fibers[36] and LB Films (Prepared at 20 °C and 20 mN/m)

		multilayers			
polymer	fiber *d*/Å	initial	annealed	*Z*	*E*
P2[a]	42.3	48.5	43.0	no	40−45
P4[b]	41.6	46.5 ± 0.8	42.0	no	42.1 ± 4.2
P6[a]	43.7	49.2	43.7	no	no

[a] Schmidt.[36] [b] Geue.[37]

The liquid crystalline order is supported by the X-ray diffraction patterns of fibers, which resemble those of smectic liquid crystals, without any indication of a columnar order. The spacings compiled in Table 3 are very similar for the polyglutamates with different spacer lengths. The spacings of 41.3−43.7 Å indicate layered structures of tilted or interdigitated side chains.

Although the length of the side chains for the photochromic polyglutamates and for the polyglutamate with the biphenyl side chains are very similar, the spacings are very different (>41 Å compared to 31.3 Å[20]). The calculated difference in the extent of the side chains (C_6 compared to C_2) of 4.8 Å does not correspond to the observed change in spacings. This fact and the increasing splitting of the amorphous halo in the diffraction pattern suggests a decreasing angle between the mesogenic side chains and the polymer backbone with increasing length of the flexible spacer. A parallel arrangement of the two different mesogenic moieties—the stiff rod-like polypeptide helices and the mesogenic azobenzene moieties of the side chain—should be thermodynamically favorable within the supramolecular assembly. In this way the rod-like polypeptide backbone and the azobenzene groups should come to a more parallel orientation, causing higher stability of the mesophase in P6. However, a sufficiently long and flexible spacer is required for such ordering. The short ethylene spacer of P2 results in an arrangement of the side group closer to a perpendicular orientation with respect to the backbone, causing the decrease of phase stability and the increase of the glass transition temperature.

Thermotropic and Optical Properties of LB Multilayers. The optical properties of the LB multilayer assemblies modified due to the photoisomerization and the supramolecular arrangement of the *E* azobenzene side groups are characterized by the wavelength dependence of absorbance, its orientational direction, and the distribution in different states established on UV or vis irradiation and upon annealing, respectively.

Initial LB Multilayers. The UV/vis absorbance spectra of the polymers in chloroform and those of the initial LB multilayers are compared in Figure 5. Since the preparations of the solutions and LB films were carried out under red light conditions, the azobenzene moieties exist to 100% as *E* isomers. The maxima at 348 nm are equal for all polymers in solution. However, the absorbance maxima of the LB multilayers are hypsochromically shifted to approximately 329 nm and different shoulders can be observed. This shift of the absorbance maxima suggests a “face to face” arrangement of *E* azobenzene moieties in dimers or clusters (H-aggregates). Furthermore, the absorbance of azobenzene chromophores is much smaller in the case of the LB films compared to those of the same number of chromophores in solution, as shown in Figure 5. This is due to the diminished extinction coefficient of the aggregated chromophores[50] and the out-of-plane orientation of the chromophores due to the hairy rod deformation.[33,38] The absorbance of the initial LB films increases with the spacer length. This is observed although a comparable extent of aggregation is established in the initial LB films of all three polymers. Thus, the differences in the absorbance arise from a different out-of-plane orientation of the azobenzene side groups. The higher absorbance with increasing spacer length suggests, in agreement with only a very small increase in the layer spacing of P2 (determined by the X-ray diffraction experiment; see Table 3) a more planar orientation of azobenzene side groups caused by the higher flexibility of the hexamethylene spacer. The longer spacer allows an arrangement of the main chain helices and the mesogenic side groups in an angle smaller than that for the short ethylene spacer of P2.

The polarized UV/vis spectra demonstrate that the azobenzene side groups are preferentially oriented in the dipping direction, as shown for a P4 film with 80 layers in Figure 6. The analysis of the spectra gives the direction of the preferred orientation and the spectroscopic degree of order of the azobenzene chromophores. The dichroic properties of the films result from the azimuthal orientation of the azobenzene groups toward the main chain helices. On the basis of the wavelength dependence of the spectra the extent of aggregation is determined by means of the procedure described in ref 33. The data for the total value of absorbance at 348 nm (“isolated” chromophores), the extent of H-aggregation, and the spectroscopic degree of order for the azobenzene side groups at 348 nm are summarized in Table 4 for all three polymers in the different processing states.

The polar diagrams in Figure 7 illustrate the angle dependence of the in-plane absorbance of the films in all established states for the polyglutamates with dependence on the spacer length. They demonstrate that in the initial LB films the azobenzene moieties are preferentially oriented in the dipping direction. The initial degree of order is quite similar for the LB films of all polymers. However, the absorbance increases with increasing spacer length.

The angle dependence of the absorbance maxima and the spectral analysis of the band structure demonstrate that the degree of aggregation depends on the orientation with respect to the backbone (Figure 8). The formation of H-aggregates is more pronounced in the direction of the backbone helices, whereas azobenzene moieties with increasing tilt angle up to a perpendicular arrangement exist preferentially as isolated chromophores. Thus, the less ordered chromophores are also less H-aggregated species.

Annealed LB Layers. The original LB multilayers were annealed at 95 °C, a temperature above the glass transitions at which bulk samples of all three polymers exist in the liquid crystalline state. On annealing, the spacing characteristic of the stressed bilayer structures established by the LB procedure is irreversibly lost, but new lamellar structures with much smaller spacings and a more symmetrical arrangement of the side groups are established, as determined by the X-ray diffraction (see Table 3).[32,36,37] The spacings found for the annealed LB films of 42.0−43.7 Å agree excellently with those of the liquid crystalline bulk structures for all three polymers (41.6−43.7 Å). These results suggest that the annealing process effects a relaxation of the constrained LB multilayer with the deformed hairy rods and enables

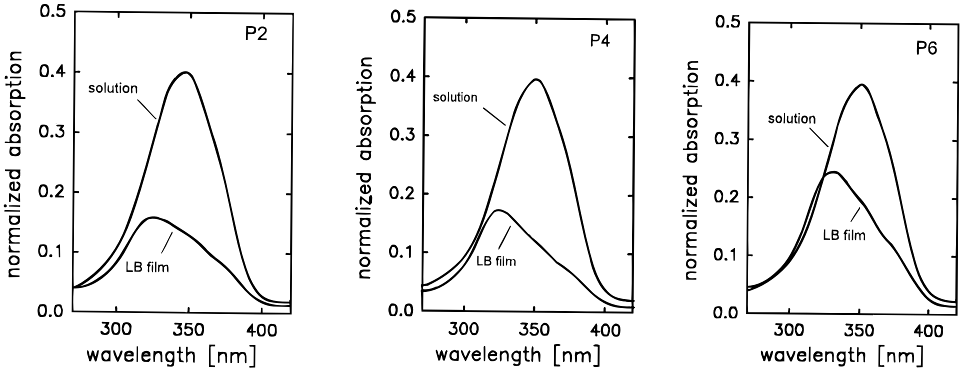


Figure 5. Absorbance spectra for initial LB layers of P2, P4, and P6 with 80 layers and for the same polymers in $CHCl_3$ (normalized to 1016 azobenzene moieties/cm^2).

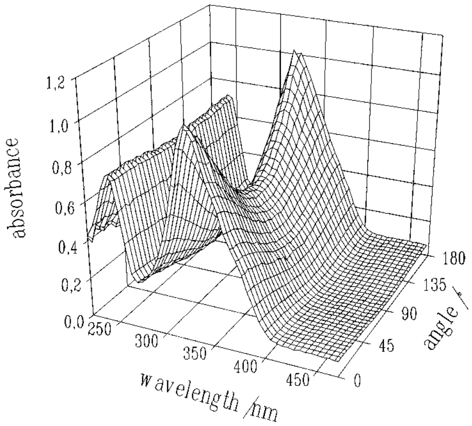


Figure 6. Angular-dependent UV/vis absorbance spectrum of an initial LB film (P4 with 160 layers on silica glass).

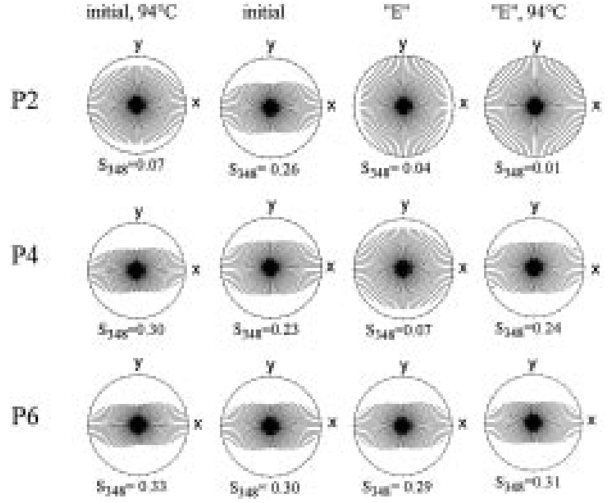


Figure 7. Angular-dependent absorbance at 348 nm of LB films built up by the polyglutamates P2, P4, and P6 in different states established upon irradiation and/or annealing at 94 °C ("annealed", "initial", "*E*", and "*E* annealed"). The dipping direction corresponds to the *x* direction, and the absolute values of absorbance are included in Table 3.

Table 4. Summaried Data of Absorbance, Degree of Order *S*, and the Amount of H-Aggregates for LB Films of P2, P4, and P6 with 80 Layers in Different States

	state of LB- layer				
polymer	initial, 94 °C	initial	"*Z*" state	"*E*" state	"*E*", 94 °C
	Absorbance (at 348 nm)				
P2	0.22	0.16	0.119	0.31	0.30
P4	0.31	0.23	0.058	0.25	0.29
P6	0.32	0.25	0.089	0.30	0.325
	Degree of Order (In-Plane)				
P2	0.07	0.26	0	−0.04	0.01
P4	0.30	0.23	0	0.07	0.24
P6	0.33	0.30	0	0.29	0.31
	H-Aggregation[a]				
P2	46	37		24	42
P4	44	43		18	40
P6	38	38		34	41

[a] Calculated according to ref 33 at 323 nm.

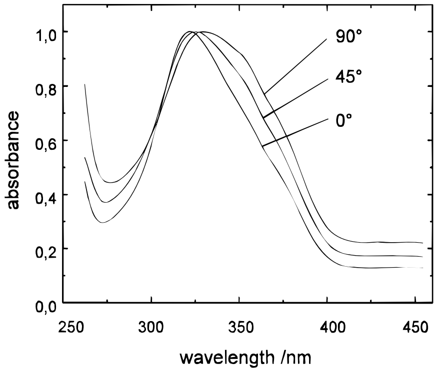


Figure 8. Normalized angular-dependent absorbance of an initial LB multilayer of P4 in 0, 45, and 90° positions to the dipping direction.

the polymers to adapt the bulk structure. In the case of LB films the parallel alignment of the hairy rods is preserved. Considering the smaller intensities and broad distribution of the Bragg peaks it can be concluded that the annealed samples are less ordered than the initial multilayers.

Upon annealing, the UV/vis absorbance of the azobenzene moieties in P4 is increased to 171% of the initial value and that of P6 to 131%. The degree of order for the in-plane orientation is improved too. Thus, the order parameter increases to 130% for P4 and 110% for P6, respectively, but the aggregation remains constant. As shown in Table 4, P4 and P6 have similar high absolute values of absorbance and a high order parameter. Both results suggest that many more azobenzene chromophores achieve a more perfect in-plane arrangement in the direction of the main chain helices.

However, a quite different behavior is found for P2. Upon annealing, the absorbance is increased to 143%, but its total value is much lower compared to P4 and P6. In contrast to the other samples the orientational order of P2 is dramatically decreased to 26% of the initial value. Since the annealed P2 film shows the highest extent of H-aggregation, the increased absorbance must be exclusively caused by a reorientation process reducing the out-of-plane orientation and re-

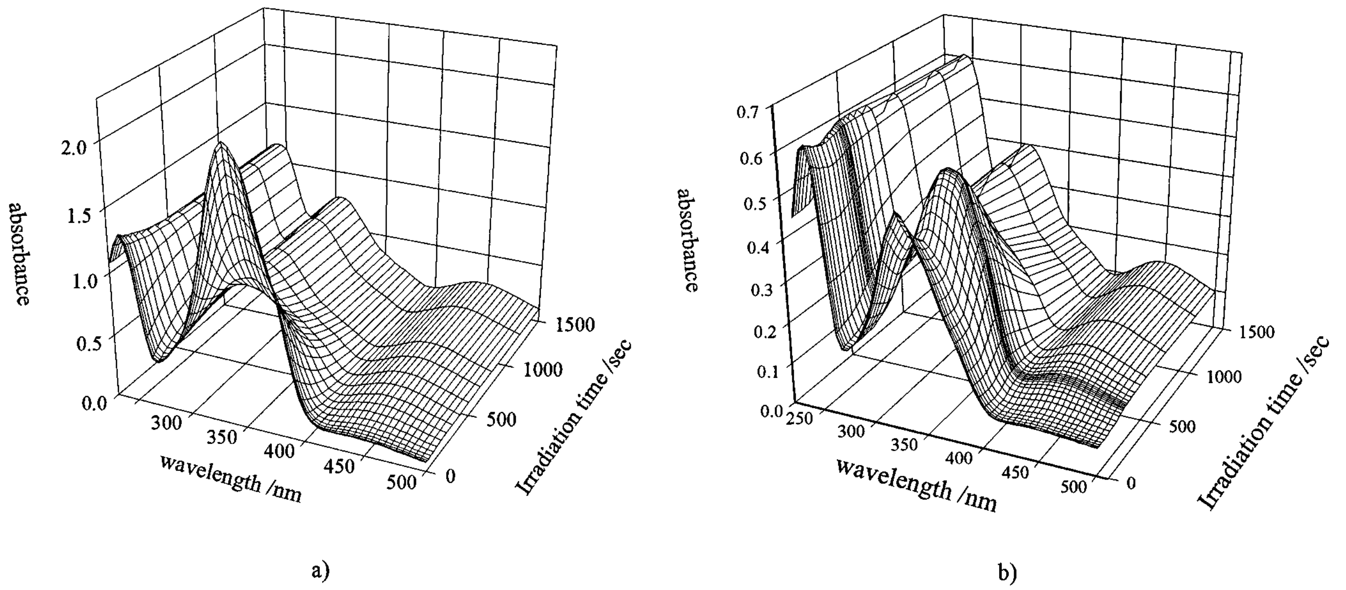


Figure 9. Spectra of absorbance of a P4 spin-coated film (a) an a multilayer (b) dependent on the irradiation time ($\lambda_{ex} = 365$ nm).

sulting in a broad orientational distribution. Thus, the self-organization process decreases the out-of-plane orientation in the LB films of all three polymers, but in contrast to P4 and P6, where the average angle between the polypeptide rod and the azobenzene side groups decreases, this angle increases to approximately 90° in P2. This results in a very weak development of its orientational direction toward the main chain helices. The significantly smaller absorbance reflects the different arrangement. But, in the case of P4 and P6 the chromophores have to be tilted toward the polypeptide rods, causing the high in-plane anisotropy.

"Z" Films. The irradiation of the polymers in solution with UV light (365 nm) establishes a photostationary state with approximately 95% *Z* isomers. The kinetics of the photoisomerization in solution is characterized by a uniform decrease of absorbance at the $\pi-\pi^*$ band (348 nm) and an increase of the $n-\pi^*$ band (440 nm).

A uniform decrease of the $\pi-\pi^*$ band is found for the spin-coated films, too (see Figure 9a), but a completely different behavior is found if the LB films are irradiated. Surprisingly, the irradiation causes a significant increase of absorbance in the range of the $\pi-\pi^*$ transition after an initial decrease (see Figure 9b).

The transient increase is observed although the photoisomerization takes place as demonstrated by the increasing absorbance of the *Z* isomers at 440 nm. Simultaneously, the maximum of absorbance of the films is bathochromically shifted from 325 to 345 nm. The new maximum corresponds to that of "isolated" azobenzene moieties. No isosbestic points can be found. This indicates that besides the isomerization additional processes take place upon irradiation. Figure 10 compares the spectra of a P4 film in its initial state, the transient minimum and maximum, as well as in the "*Z*" state. The bathochromic shift of the maximum absorbance and its transient higher value are significant.

The complex kinetics is shown in Figure 11 by plotting the absorbance of a P4 film on continued irradiation against the time. Before the new maximum of absorbance is established, an initial decrease is observed due to the photoisomerization. The transient increase of absorbance, however, cannot be understood in terms of a monomolecular photoreaction of "isolated" *E* azobenzene chromophores.

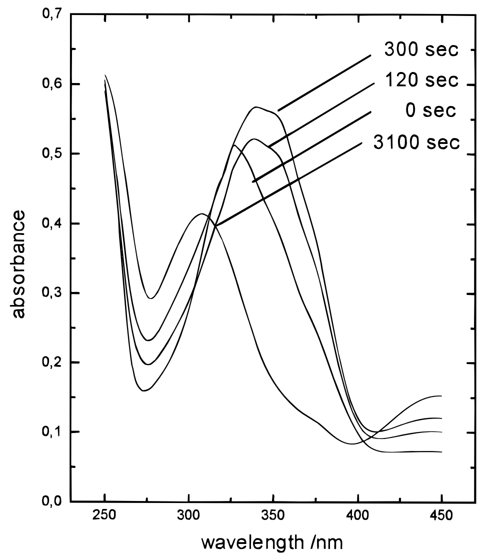


Figure 10. Absorbance of LB multilayer P4 at 348 nm dependent on the UV irradiation procedure with 365 nm light (initial film, temporal minimum, temporal maximum and "*Z*" film).

The analysis of the aggregation by the band-separated areas of the spectra according to Figure 4 shows a dramatic decrease of H-aggregates in the first 500 s connected with a significant increase of the absorbance of the isolated species.

Upon irradiation not only the aggregation but also the orientational order of the chromophores is changed, as can be seen in Figure 12.

There is a distinct dichroic ratio in the initial state, but the orientational order is strongly decreased within the first 500 s, which corresponds to the transient minimum of absorbance. The transient maximum is connected with a further small decrease of dichroism, which is completely lost in the "*Z*" state. In addition, the figure illustrates that the average absorbance at 348 increases in the first period although the number of *E* isomers is decreased due to the photoisomerization.

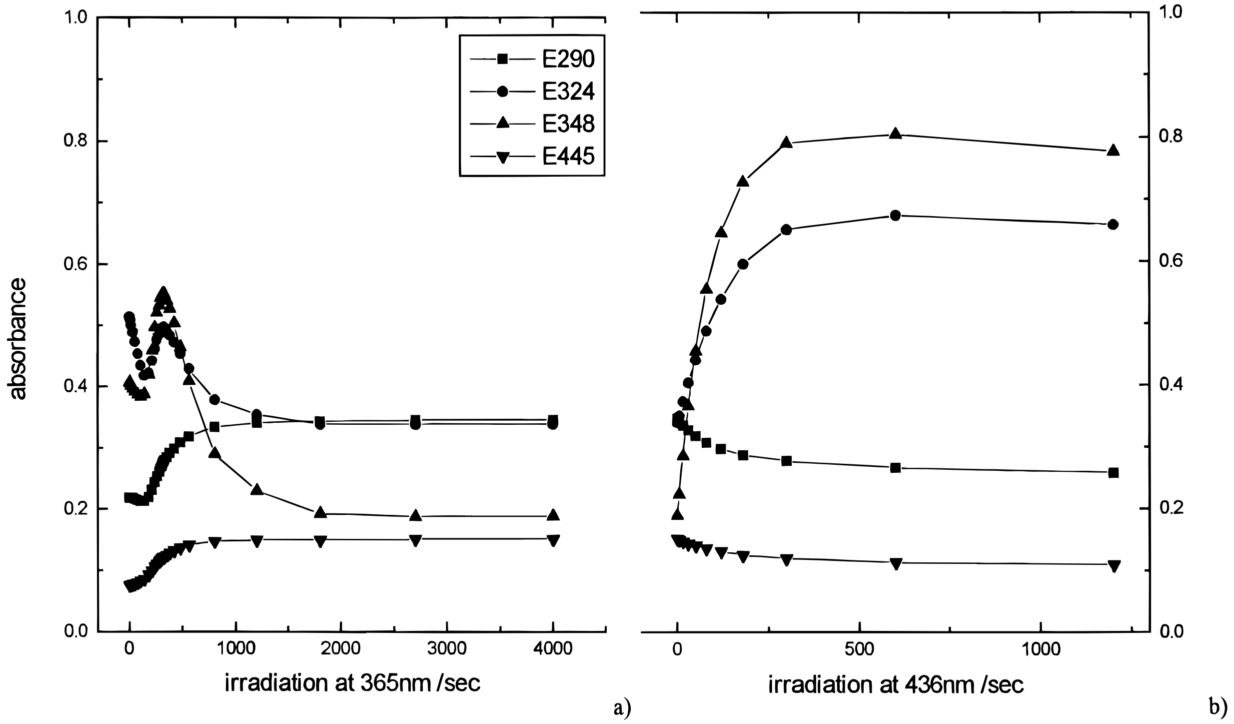


Figure 11. UV/vis absorbance spectra of an LB film of polymer P4 (a) on UV irradiation (365 nm) and (b) following vis irradiation at 436 nm.

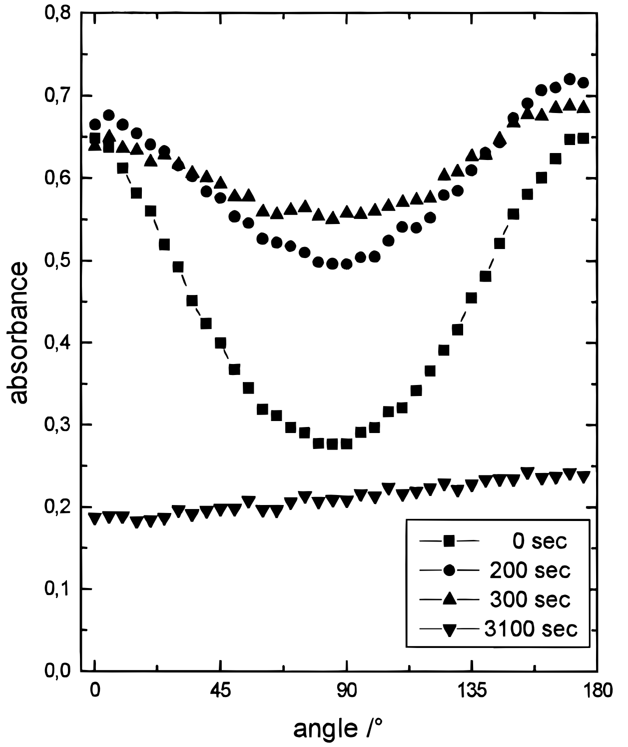


Figure 12. Angular dependence of absorbance at different times of UV irradiation (according to Figure 10).

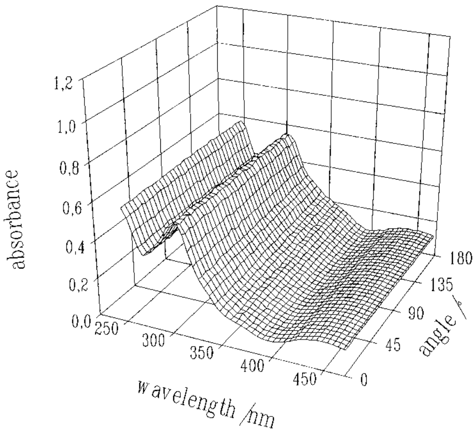


Figure 13. Angular-dependent UV/vis absorbance spectrum of an LB film for P4 in its "Z" state with 160 layers on silica glass.

All results together suggest that this spectral change is caused by a photoinduced destruction of the H-aggregates due to the *E*−*Z* photoisomerization. The bathochromic shift and transient increase of absorbance are caused by releasing nonaggregated *E* azobenzene moieties. The concomitant reduction of the out-of-plane orientation contributes also to the increase of absorbance.

A similar spectroscopic behavior is observed in the case of all homopolymers, but related copolyglutamates with isolated, nonaggregated azobenzene side groups do not show such a behavior.[51,52]

The polymers P2 and P4 as spin-coated films have maxima of absorbance at 345 nm, indicating nonaggregated chromophores. On irradiation the behavior of these films is quite similar to that of the copolymers and those of the polymers in solution. As shown in Figure 9a, the UV irradiation effects a uniform decrease of absorbance. A temporary increase and a bathochromic shift of $\pi - \pi^*$ absorbance are not observed in the disordered films. Thus, the effect of photoinduced deaggregation seems to be related to the preferred existence of H-aggregates of photochromic moieties in ordered systems.

On continued irradiation the steady state is established with a high ratio of *Z* to *E* isomers. The layered structure of the deformed hairy rods or the "annealed *E*" state is always lost as consequence of the photoreaction and the subsequent relaxation, as indicated by the disappearance of the Bragg peaks (see Table 3). The

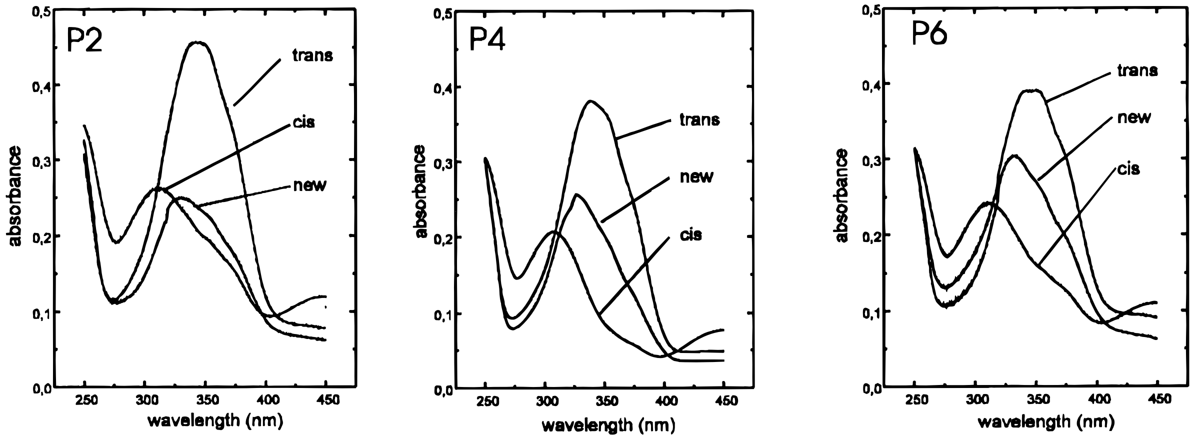


Figure 14. Absorbance of the LB films of P2, P4, and P6 with 80 layers in the initial, "*Z*", and "*E*" states.

optical properties of the films are similar for all three polymers with maxima of absorbance at 310 and 450 nm, which have comparable values of absorbance. The LB films in the steady state ("*Z*" films) are optically isotropic, indicating that any in-plane orientational order of the azobenzene moieties is lost (Figure 13).

"***E***" **Films.** Subsequent irradiation with vis light (488 nm) establishes a steady state, in which the rod-like *E* azobenzene moieties are dominant to approximately 85%. The related part of the *Z* isomers represents a much smaller disturbance of the ordered system. A new lamellar structure appears in the LB films of P2 and P4 as a result of the rebuilt rod-like azobenzene side groups. But it is much less developed than that of the original LB multilayer and has a much smaller periodicity.[35] However, the peak intensity of the new spacing increases upon annealing. Irradiated films of the polymer P6 do not show a Bragg peak, but upon subsequent annealing a new lamellar structure is observed. In all cases the spacings of the established order are very close to those of the LB films which were annealed without irradiation and to those of the bulk phases.[36,37]

Three isosbestic points can be observed in the course of the photochemical *Z*−*E* isomerization. This fact suggests that in contrast to the *E*−*Z* photoisomerization the *Z*−*E* isomerization occurs as a uniform reaction of nonaggregated chromophores. Figures 14 and 10b show that the absorbance of the "*E*" films is significantly increased in comparison to the original multilayers. In the case of P2 the absorbance rises up to 200% of the initial value. In P4 and P6 films the corresponding increases are much smaller with 125% and 120%, respectively. Compared to the original multilayers, the maxima of the spectra are bathochromically shifted from 325 to 348 nm.

The systems show big differences in the orientational order, too. Thus, the dichroic properties of the three LB films are completely differently modified as a result of the photoisomerization cycle. Whereas the order parameter in P6 films remains nearly constant, that of P4 is decreased to 30% of the initial value. In the case of P2 the preferred orientation of the chromophores in the dipping direction and parallel to the main chain helices is completely lost and a slight preference of the orientation perpendicular to the main chain helices is found ($S = -0.04$). This is visualized by the change of the sign in the order parameter. In all cases the degree of the photochemically established order is smaller compared to any other state. Furthermore, the aggregation is significantly decreased in films of P4 to 42% and in P2 to 64% compared to the initial multilayers, but it is only slightly influenced by the irradiation cycle in the case of P6 LB films.

On the molecular level the *Z*−*E* photoisomerization rebuilt approximately the initial state of the photochromic moieties, but the supramolecular structure and the resulting optical properties are completely different as a result of the irradiation cycle compared to those of the initial LB multilayers. Furthermore, with dependence on the spacer length quite different supramolecular ordered states, especially concerning the orientational order of the side groups, are photochemically established for the three polymers.

Annealed "***E***" **Films.** On annealing the "*E*" films the last *Z* isomers react thermally back to rod-like and less polar *E* isomers. Furthermore, the annealing in the viscoelastic range of LCP's above the glass transition accelerates the structural response to the thermodynamic equilibrium of the new steady state by the increased mobility of the side chains. In the case of P6 films the absorbance, the order parameter, and the molecular aggregation are increased slightly. On the other hand in the case of P2 the aggregation is increased from 64% to 113% in relation to the initial value. This process is connected with a slight decrease of absorbance. The direction of the orientational order is once more changed and a very weak orientation toward the direction of the helices is established. Except for the increase of the aggregation of P2 there are no dramatic changes for these two polymers upon annealing of the irradiated LB films. Although the photochemically established structures of P2 and P6 are quite different, both seem to be very near to the state of equilibrium. This is not the case for the irradiated films of P4, since annealing causes strong changes. Besides the increase of the aggregation, which reaches the level of the initial state, the orientational order of the side groups is changed dramatically. The order parameter increases from 30% of the initial state to 104% (see Table 4). In this way the photochemical induced structure of the LB film after an irradiation cycle characterized by a small order parameter and less extended aggregation of the chromophores was changed into an arrangement of strongly aggregated chromophores, which have a preferred orientation in the direction toward the main chain helices. In contrast to P4 the annealing process stabilizes in P2 films a non-tilted orientation of the side groups. This is connected with the loss of any in-plane orientational order of the azobenzene moieties.

After annealing, the absorbance and the degree of aggregation are very similar for the films of all three

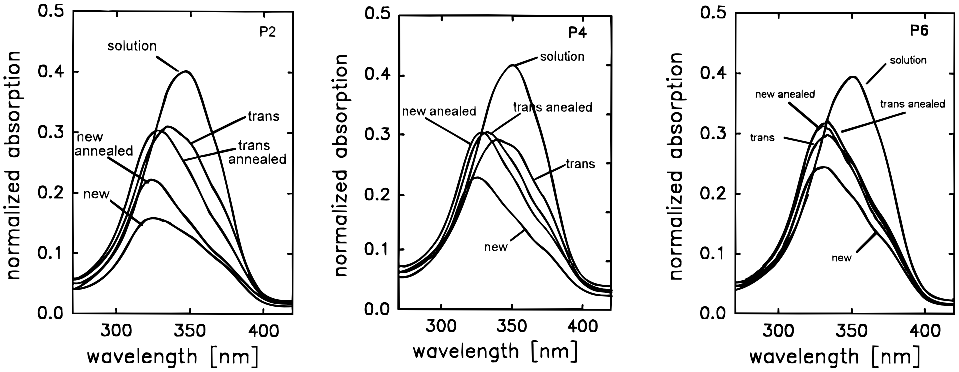


Figure 15. Comparison of the UV/vis spectra of absorbance of LB films P2, P4, and P6 in different states ("annealed", "initial", "*E*", and "*E* annealed") and the normalized spectra for the same polymers in solution.

Table 5. Birefringence of a P2 Film with 400 Layers in Different States

state of LB layer	Δn (at 633 nm)	S (at 440 nm)	direction (deg)
"initial"	0.042	0.22	0
"Z"	0	0	
after thermal $Z \rightarrow E$	0.021	0.17	90

polymers, but the orientational order of the azobenzene side groups is quite different.

Birefringence. The difference in the optical way of light was measured using an Ehringhaus compensator to calculate the birefringence in consideration of the thickness of the samples. Thus, the birefringence of a 2.002 μm thick LB film of P2 (1.001 μm on each side of the substrate) was detected in different processing states. The birefringence of the initial film was $\Delta n = 0.042$ (see Table 5). In agreement with the dichroic properties the optical axis was directed in the dipping direction. UV irradiation causes a complete loss of the birefringence, which agrees with the erasing of the UV/vis dichroism in the "Z" films. On the other hand the FT-IR dichroism, which is related to the orientational order of the main chain helices, is not altered by the irradiation.[31] This fact suggests that the oriented polypeptide helices do not contribute to the birefringence. The birefringence as well as the UV/vis dichroism are exclusively caused by the orientational order of the azobenzene side groups.

The birefringence of the P2 film reappears after thermal $Z-E$ isomerization and storage in the dark for 24 h at room temperature ($n = 0.021$). However, in contrast to the initial film the direction of the optical axis is directed perpendicular to the main chain helices. This finding is in agreement with the UV/vis measurement which reveals a perpendicular orientation of the chromophores to the main chain helices (see Figure 6). This experiment shows that the optical anisotropy of initial stressed LB films of hairy rod polyglutamates can be modified by nonpolarized light via temporary photochemical variations of the intermolecular interaction.

Discussion

The polyglutamates substituted with azobenzene side groups are polymers of the hairy rod type, which combine the ability to form LB layers with thermotropic properties. The structure of the initial LB multilayers is characterized by well-ordered bilayers of deformed hairy rods. The deformation is developed by the interaction of the hairy rods with the polar water surface and the applied surface pressure and it is retained in the transfer process. Structural peculiarities of these LB multilayers, which strongly influence their photochemical behavior, are caused by the nematic-like orientational order of the hairy rods in each layer and the fact that the macroscopic alignment of the main chain helices in the dipping direction is preserved in all processing states. The supramolecular structure of the initial LB multilayers is similar for all studied polyglutamates. The hydrophobic azobenzene side chains are nonsymmetrically arranged around the polypeptide helix and tilted toward the main chain rods. But the angle between the backbone and the azobenzene side groups is related to the length of the flexible alkyl spacer. In the case of a longer spacer the rod-like *E* azobenzene moieties tend to be oriented more parallel to the α-helical backbone.

The supramolecular structure of the LB films can be manipulated in two different ways by changing temporarily the intermolecular interactions of the side groups. The first way uses the thermotropic properties of the polymers, inducing a new, thermodynamically stable structure upon heating. The second one reduces photochemically the interactions of the side chains due to the photoisomerization of the azobenzene moieties at room temperature. In both cases the well-ordered structures of the initial multilayer are destroyed and less ordered states are established, which correspond to those of the liquid crystalline bulk phases. With dependence on the glass transition temperature of the polyglutamates the photoinduced disorder is frozen-in on irradiation, but on subsequent annealing, the polymers relax to the thermodynamically stable liquid crystalline order.

The structures of P2, P4, and P6 LB films in the different processing states differ mainly in the orientational order of the side groups and the extent of the aggregation. The supramolecular order established due to the photoisomerization cycle or by the thermotropic self-organization of the azobenzene side groups is controlled by the enthalpic stability of the mesophase and the dynamic properties of the polymer. In this system both the ordering tendency and the mobility are modified by the length of the spacer. In this way the spacer length determines the extent of the H-aggregation and the orientational order. The relation between photochemical modification and different mechanisms of self-organization due to molecular aggregation and liquid crystallinity, which determines the optical properties of the films by photoinduced reorientation processes, will be discussed in more detail.

Aggregation. The hypsochromic shift of the maxima and the decreased absorbance suggest the self-association of the azobenzene chromophores to dimers or clusters, in which the transition moments are parallel oriented in a head-to-head arrangement (H-aggregate). The spectral changes are caused by an exciton splitting, which results in an allowed high-energy transition and a forbidden low-energy one according to the exciton model introduced by Kasha.[53−55]

The molecular exciton model describes the excited state resonance interaction between molecules in van der Waals aggregates. The interpretation of spectrophotometric observation using this model results in a better understanding of the precise molecular ultra structure within these lamellar systems. The fact that almost no H-aggregates are formed in solution, nor in the spin-coated films, shows that there is no tendency for self-association in the absence of external forces. However, the self-organization to H-aggregates is frequently encountered in microheterogeneous systems such as LB multilayers.[56,57,63] liquid crystalline polymers,[58] and guest−host mixtures.[59,60] In such ordered systems the exciton interaction is stimulated by the high local concentration combined with enforced orientation and geometrical packing as well as hydrophobic/hydrophilic interaction. In the LB multilayers of the hairy rod polyglutamates such aggregates of rod-like azobenzenes are formed in the hydrophobic and well-organized layers of the side chains. The spectral differences reflect the intermolecular interactions of the chromophores and their relative orientation to each other.

In the initial LB multilayers of all three polymers a comparable extent of chromophores exist as H-aggregates. On annealing, the bilayered structure is destroyed. The amount of aggregated species remains constant in the case of P4 and P6, but a further increase of H-aggregation is found in the P2 films. This is connected with a reorientation of the side groups to a lower orientational order.

The irradiation with UV light results in a very unexpected spectral change, which is in contrast to the behavior of the photochromic polymers in solution and as spin-coated films. The results are interpreted in such a way that the transient increase of $\pi-\pi^*$ absorbance, the bathochromic shift of the maxima and the significantly higher $\pi-\pi^*$ absorbance of the "E" films are caused by the efficient photoinduced destruction of the H-aggregates and a concomitant destruction of the out-of-plane orientation. The changed geometrical shape and increasing polarity of a small amount of the photoisomerized azobenzene moieties modify the intermolecular interactions within the aggregates. By this way the $E-Z$ photoisomerization triggers a destruction of the aggregates and the release of nonaggregated E isomers (see Figure 10). The temporary increase of absorbance demonstrates that more "isolated" E chromophores are formed than azobenzene moieties undergo photoisomerization (see Figure 9 and 10).

The aggregation is completely destroyed in the "Z" films, but H-aggregates are restored after $Z-E$ isomerization. In the case of polymer P6 the strong ordering tendency and the higher mobility cause an efficient simultaneous reaggregation. The extent of the aggregation in the "E" film is nearly unchanged compared to the initial LB film.

In the case of P2 and P4 films the extent of aggregation is reduced after an irradiation cycle ("E" film) compared to the initial LB films. In these films the deaggregation is connected with a loss or decrease of the orientational order due to the reorientation of the side chains. The increased absorbance of the "E" films compared to the initial films (see Figure 10b) is due to deaggregation and increasing in-plane orientation of the azobenzene side groups. But only on subsequent annealing are the aggregates rebuilt in P2 and P4 on the same level like in P6. That means the extent of aggregation is independent of the different orientational order of the side groups.

The preferred formation of H-aggregated clusters and their efficient photoinduced destruction stimulated by the photochemical variation of a small number of stacking chromophores seems to be a very common phenomenon in the photochemistry of ordered assemblies and solids. Recently, we have found that such photoinduced deaggregation takes place in liquid crystalline guest−host systems,[59,60] in the glassy and viscoelastic state of liquid crystalline polymers,[58] and in LB multilayers of amphotropic polyacrylates.[15−18,64] Several photochromic moieties like azobenzene, stilbene, or cinnamic acid derivatives show this effect.[33,57−59] Similar results are reported by Hoyle[61] and Whitten.[62]

A synergistic effect of liquid crystallinity and molecular aggregation can be suggested because of their mutual stabilization.

But up to now the contribution of such apolar association in establishing liquid crystalline order is not understood. Concerning their photoinduced destruction, the H-aggregates of photochromic moieties are much more sensitive to the photochemically changed intermolecular interaction than the liquid crystalline order.

The influence of H-aggregation and -deaggregation on the dynamic properties detected by photoorientation upon irradiation with linearly polarized light will be discussed in a forthcoming paper.

Orientational Order and Liquid Crystalline Properties. The only difference in the molecular structure of the three polyglutamates is the length of the flexible alkylene spacer between the mesogenic azobenzene side group and the rod-like, α-helical polypeptide backbone. The two mesogenic moieties are more decoupled by a longer spacer, in this way both moieties of the combined liquid crystalline main and side chain polymers can be packed more perfectly. A parallel arrangement of the stiff rod-like polypeptide helices and the mesogenic azobenzene moieties should be thermodynamically favorable in agreement with the general behavior of bridged bimesogenic liquid crystals or combined main and side chain LCP's. By this reason, the increased spacer length causes the increase of the enthalpic stability of the mesophase, changes the temperature range, and decreases the glass transition temperature. Thus, the ordering tendency and the dynamic properties of the thermotropic polyglutamates are modified by the spacer length.

In the LB films the modification of the in-plane and out-of-plane orientational order of the azobenzene side groups in relation to the macroscopically aligned polyglutamate helices is the most significant change on irradiation and annealing. The established order is quite different for the three polymers and depends significantly on the spacer length.

The disturbance caused by the $E-Z$ photoisomerization destroys the side chain order, whereas the photoinduced disorder is quite similar in the "Z" films for all three polymers. On the molecular level the subsequent $Z-E$ photoisomerization rebuilt the E azobenzene moieties. At room temperature states are established in which the films are far from the thermodynamical equilibrium of the polymers. The structural response of the LB assemblies on the disordering effect is quite

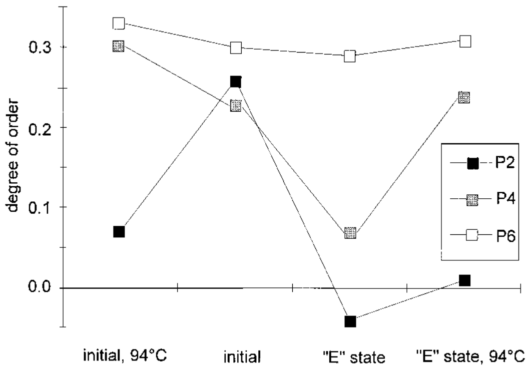


Figure 16. Summary of the degree of order in the different states for P2, P4, and P6.

different for the three polymers. Thus, as a result of the UV and vis irradiation cycle quite different supramolecular structures are established, although the same molecular reactions took place with comparable efficiencies. The results demonstrate that the subsequent structural relaxation depends on the structure of liquid crystalline order, the different ordering tendency—the enthalpic stability of the mesophase is a scale for this—and the different dynamic properties of the liquid crystalline polyglutamates.

Polymer P6 with the hexamethylene spacer is characterized by the smallest angle between the side chain and the main chain helix in the initial LB film, in the films modified by light and on annealing, and in the liquid crystalline bulk phase. Annealing and irradiation result in reducing the out-of-plane orientation of the azobenzene side groups, which increases the absorbance and the orientational order in the direction toward the polypeptide backbones. The higher absorbance and the higher in-plane optical anisotropy compared to those of the other polymers are due to the smaller tilt angle.

Starting from the less ordered "*Z*" films, the supramolecular structure of P6 is restored at room temperature. The interaction between the polypeptide rods and its mesogenic side groups act as an aligning force for the orientation of the azobenzene chromophores in P6. The efficiency for parallel orientation depends on the decoupling of both moieties by the spacer or, more generally, the stability of the liquid crystalline order. In P6 simultaneously to the *Z*—*E* photoisomerization the H-aggregates are formed and the orientational order of the side groups is established. This behavior of P6 is different in comparison to those of the other polymers and should be caused on one hand by the high enthalpic stability of the liquid crystalline order and on the other hand by the higher mobility of the hexamethylene spacer. The absorbance, aggregation, and degree of orientational order are very similar in all P6 films with *E* azobenzene side groups. These films are very stable against all external distortions (see Table 4 and Figure 16).

The short ethylene spacer in P2 and with that the related low ordering tendency cause a quite different orientational order of the azobenzene chromophores compared to those of P4 and P6. In the case of P2 irradiation and annealing destroy the initial order of the LB film and both procedures result in a nearly isotropic distribution of the side chains (see Table 4 and Figure 16). In the case of P2 only the stimulated formation of the H-aggregates can be observed on annealing, because any preferred orientational order of the side groups does not exist in the photoinduced and annealed films. The behavior of P4 takes an intermediate position. The "*E*" films are more similar to that of P2, but the annealed films are quite similar to P6 films. In contrast to P2 the angle between the side group and the main chain helix is decreased on annealing, in this way the in-plane orientational order in the direction of the hairy rods is increased. On the other hand the UV/vis photoreaction cycle induces a disorder comparable to that of P2. In the case of P4 and P2 this photochemically induced disorder is frozen-in at room temperature. Subsequent annealing of the P4 film restores the preferred orientation of the side groups in the direction of the main chain helix and the molecular aggregation (see Table 4 and Figure 16).

The strong influence of the liquid crystalline order and of the extent of the photoinduced disorder on the structural relaxation can be recognized by comparing the results for these homopolymers with those of a copolyglutamate with only 16% azobenzene moieties. In this case the chromophores are not aggregated. The isolated azobenzene moieties are separated from each other by flexible alkyl chains.[51] The UV irradiation does not destroy the initial layered structure of the LB film, but a thermal relaxation of the structure is observed. The changes of the optical properties upon irradiation, especially the orientational order of the side groups are fully reversible. The photoisomerization takes place as a local process without great impact on the order of the LB film.

Our recent studies concerning the photochemical modification of aligned films of liquid crystalline polyacrylates with azobenzene side groups show a similar dependence on the spacer lengths. The orientational order increases or decreases depending on the enthalpic stability of the liquid crystalline order of the polymers in their glassy state.[9,45] This study confirms the conclusion that the supramolecular order of LB films of these thermotropic polypeptides established due to irradiation and/or annealing is determined by the enthalpic stability of the mesophase and the dynamic properties of the polymers.

Conclusion

The results emphasize the dominant role of an ordered environment for the controlling photoreactivity and photochemically stimulated reorientation processes. Molecular photoreaction can be suppressed completely in the case of stiff cages or inefficient free volume. In the studied case it was shown that the influence of the environment is not restricted to the static effect of stiff cages. In liquid crystalline systems, which combine supramolecular order and anisotropic mobility, dynamic cage effects work. In all studied polymers the photoisomerization takes place in a quite similar way on a molecular level. However, the change of supramolecular structure and, thus, the resulting optical properties are changed completely differently. The ordering tendencies of the thermotropic polymers control the cooperative reorientation processes in the supramolecular assemblies. The relation between molecular photoreaction and the ordering tendency of systems seems to be a quite general phenomenon in supramolecular photochemistry.

In forthcoming papers we will discuss the interaction of these ordered polyglutamate LB multilayers with linearly polarized light and the relation between the tendency of self-organization and photoreactions in other LC systems.

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