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Langmuir–Blodgett Films of Photochromic Polyglutamates. 4. Spectroscopic and Structural Studies on Langmuir–Blodgett Films of Copolyglutamates Bearing Azobenzene Moieties and Long Alkyl Chains†

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ABSTRACT: Langmuir–Blodgett (LB) films of photochromic poly(5-(4-phenylazo)benzyl L-glutamate-*co*-5-(4-hexadecyloxy)benzyl L-glutamate) were investigated by means of FT-IR, GIR, and UV–vis spectroscopic methods and by X-ray reflection. A preliminary model for the structure and the structural changes upon irradiation is deduced. The structure is characterized by deformed "hairy rods", i.e., with a nonsymmetrical distribution of the side chains around the main chain. The hairy rods are arranged in layers with the main-chain helices preferentially oriented in the dipping direction. The deformation is a result of the interactions at the air/water interface and the surface pressure applied to the monolayer and is retained in the transfer process. The chromophores in the LB film are separated from each other by alkyl chains such that no aggregation occurs. Upon irradiation there are only minor changes in the structure. Upon prolonged irradiation and/or heating of the LB film, a relaxation of the deformed hairy rods toward a more symmetrical distribution of the side chains occurs.

Introduction

Photochromic Langmuir–Blodgett (LB) films are self-organizing systems which can be controlled by light. They show interesting properties and therefore have been suggested for many applications. One of these is optical data storage.[1,2] However, certain requirements such as thermal and mechanical stability and high homogeneity have to be fulfilled for application of the LB films. Thermal and mechanical stability can be achieved using polymers.[3,4] To overcome the problems with low in-plane homogeneity due to microcrystallization,[5–7] two different approaches have been attempted, which both rely on the high mobility and high order in liquid crystalline states. One approach is to incorporate mesogenic groups into the side chains of a hydrophilic polymer.[4] In LB films of the resulting polymer the two-dimensional microcrystals can be melted without destroying the order and structure of the LB films.[8] So external forces may be used to induce large-scale ordering. The other approach is to use rigid rod polymers equipped with flexible side chains, so called "hairy rods". With an appropriate molecular architecture provided, such polymers exhibit liquid crystalline behavior[9,10] and surface activity.[11–13]

For use in a setup for optical data storage a light-interacting unit has to be incorporated into the LB film. To embed photochromic dyes into the hydrophobic part of a polyglutamate LB film was the first approach.[1,14] But these systems suffer from the relatively high mobility of the dye molecules in the layer, resulting in low homogeneity due to phase separation in the case of higher dye contents. For this reason copolyglutamates were synthesized bearing long alkyl chains and covalently bound azobenzene chromophores.[15] In fact, very homogeneous LB films of the copolymer have been obtained. The isomerization of the azobenzene moieties proceeds to a high extent upon irradiation with UV light. But in an experiment concerning the data storage ability, we failed to obtain a pattern readable by surface plasmon microscopy by writing photochemically into the LB film.[15] For this it was concluded that the isomerization of the chromophore causes only minor changes in the optical properties which are to small to be detected by this method.

In this paper we report on spectroscopic (FT-IR, UV–vis) and X-ray diffraction experiments carried out to elucidate the structure and the structure alterations of the LB films upon irradiation and to understand why there are only minor changes in the optical properties.

Experimental Section

Materials. The investigations were carried out with poly(5-(4-phenylazo)benzyl L-glutamate-*co*-5-(4-hexadecyloxy)benzyl L-glutamate) with 16 mol % of the azobenzene moieties. Synthesis, characterization, and spreading of the polymer were described earlier.[15]

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† Part 3: see ref 20.

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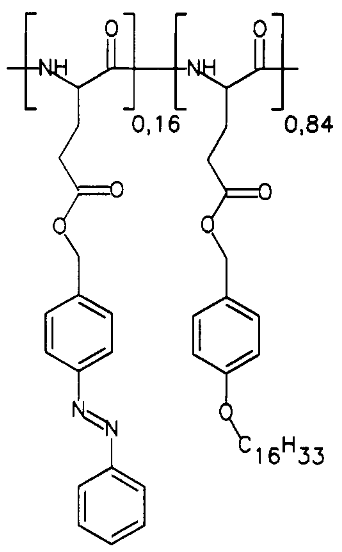


Float glass slides (X-ray), quartz slides (Hellma, Suprasil fused-silica optical windows; UV–vis spectroscopy) and silicon wafers (cut from standard (100) silicon wafers donated from Wacker Chemitronic GmbH; FT-IR spectroscopy) were used as substrates for the LB films. After rinsing with chloroform, the cleaning process included subsequent treatment with surfactants, ammonia/30% H_2O_2 (1:1), and nitric acid in an ultrasonic bath. Thus cleaned, the substrates are 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, Barnstead 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 surface area.

Irradiations were carried out using a 200-W high-pressure mercury lamp (Oriel), employing a cutoff filter to obtain light with a wavelength $\lambda > 470$ nm (Spindler and Hoyer GG 10) or a band-pass filter for light with $\lambda = 360 \pm 50$ nm (Spindler and Hoyer UG-1). A cuvette filled with distilled water was used to remove the IR radiation.

A LB film is called "new" when a dark-adapted solution is spread to a monolayer and this monolayer is transferred to a LB film under red light conditions to ensure that all azobenzene moieties are in the trans state. It is called "cis" when a "new" film is irradiated with UV light ($\lambda = 360 \pm 50$ nm) until the photostationary state is reached (about 1 min). LB films called "trans" are obtained by irradiating "cis" films with visible light ($\lambda > 470$ nm) until the photostationary state is reached (about 2 min).

The FT-IR spectra were recorded on a Bruker IFS 113 V instrument[16] using a MCT detector. For the polarization labeled $\parallel$ the substrate was oriented in the spectrometer so that the light impacted normal to the film plane and with the dipping direction (*t*; see Figure 1) parallel to the electric field vector of the polarized light ($E \parallel y$; see Figure 1). The polarization labeled $\perp$ is rotated by 90° from this direction ($E \parallel x$; See Figure 1).

UV–vis spectra were recorded on Perkin-Elmer Lambda 5 and Perkin-Elmer Lambda 19 instruments. Polarization was performed using a Glan–Taylor prism polarizer from calcite (LOT). The geometrical relations are the same as in the case of the FT-IR measurements. The order parameters were calculated by $S = A_{\parallel} - A_{\perp}/A_{\parallel} + 2A_{\perp}$ ($A_{\parallel}$ = absorption in the preferred direction; $A_{\perp}$ = absorption at 90° to the preferred direction).

X-ray reflection spectra of LB multilayers on float glass were recorded with the X-ray reflectometer (Rigaku rotating anode, Ni-filtered Cu Kα line) described in ref 17. The beam was collimated to 0.05-mm width, 1.0-cm height, and a divergence of 0.01°. The background was lower than 0.2 counts/s and, the flux on the sample amounted to 10^6–10^7 counts. The experimental reflectivity was compared with simulations of different models of the LB multilayer assemblies, calculated with the Fresnel matrix method[18] and the first Born approximation.[19]

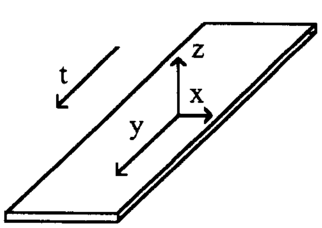


Figure 1. Geometrical relations.

Table I. Infrared Absorption Bands in Polyglutamates and Their Assignment and Orientation[24]

no.	wavenumber (cm^{-1})	band assignment	dichroic ratio[a]	direction of transition dipole moment
1	3280	N–H stretching	0.40	along the helix axes
2	2930	CH_2 asym stretching		
3	2860	CH_2 sym stretching		
4	1740	C=O stretching (ester)		
5	1653	amide I	0.47	along the helix axes
6	1558	amide II	2.2[b]	nearly perpendicular to the helix axes

[a] The dichroic ratio ($R = A_{\perp}/A_{\parallel}$) strongly depends on the geometry of the trough with regard to the size of the substrate.[23] [b] The order parameter S can be calculated from the dichroic ratio to $S = 0.36$ (according to ref 23).

Results and Discussion

Preparation of LB Films and Transfer Properties. The monolayers spread from dark-adapted solutions (azobenzene moieties are all trans) could be transferred to hydrophobic substrates under surface pressures up to 40 mN/m. The transfer were determined to be 90–97%.

FT-Infrared Spectroscopy. Transmission FT-IR spectroscopy with polarized light gives information about the orientation of chemical subunits of the polyglutamates in the *xy* plane (see Figure 1) of the LB film. The vibrational bands, their assignment, and their orientation are compiled in Table I.

In the case of orientation within the LB film, marked differences in band intensities are expected. The transmission spectra for a "new" LB film, which are depicted in Figure 2, clearly show such differences. The greater absorption in the N–H stretching (1) and the amide I band (5) parallel to the dipping direction (negative bands in the difference spectrum) and a smaller absorption for the amide II (6) (positive band in the difference spectrum) give evidence for a preferred orientation of the helices in the dipping direction. Such an orientation has been found for polyglutamates,[11,20] phthalocyaninatopolysiloxanes,[12,21] and derivatives of amylose[22] and results from the flow occurring in the transfer process.[23]

There are no significant differences between the FT-IR spectra ($\perp$, $\parallel$, ($\perp - \parallel$)) obtained from a "new" LB film and a "trans" LB film in the region of the bands compiled in Table I. Therefore it can be concluded that there are no changes in the structure and the orientation of the main chain upon irradiation.

UV–vis Spectroscopy. The absorption of the trans azobenzene chromophore is characterized by the $\pi-\pi^*$ band in the region of 323 nm and the $n-\pi^*$ transition at 440 nm. The $\pi-\pi^*$ band is diminished while the $n-\pi^*$ band increases upon trans–cis isomerization as depicted

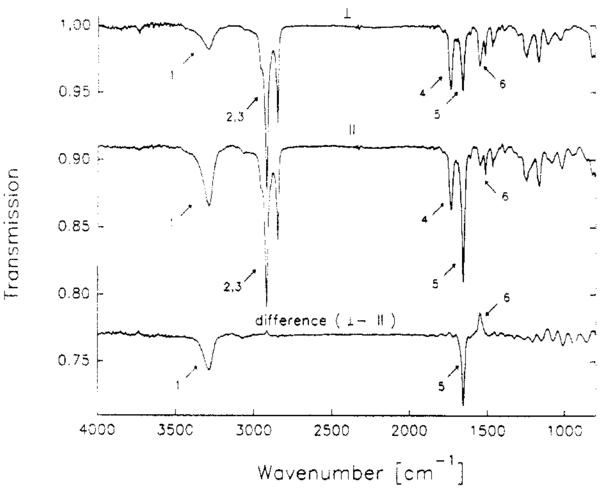


Figure 2. Polarized FT-IR spectra of a "new" LB film (80 layers); polarization parallel (∥) and perpendicular (⊥) to the dipping direction and difference spectrum (⊥ − ∥).

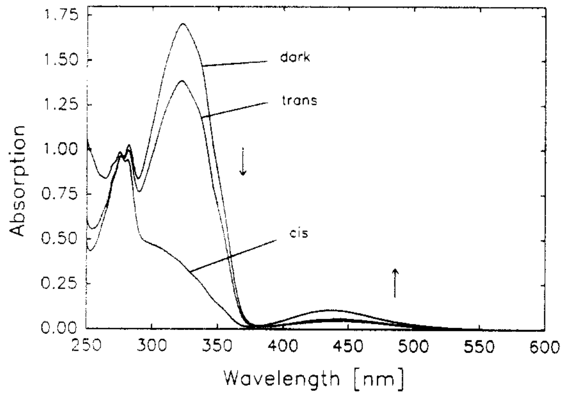


Figure 3. UV–vis spectra of a solution of the copolymer in $CHCl_3$ ($c = 5.032 \cdot 10^{-5}$ mol/L azobenzene moieties).

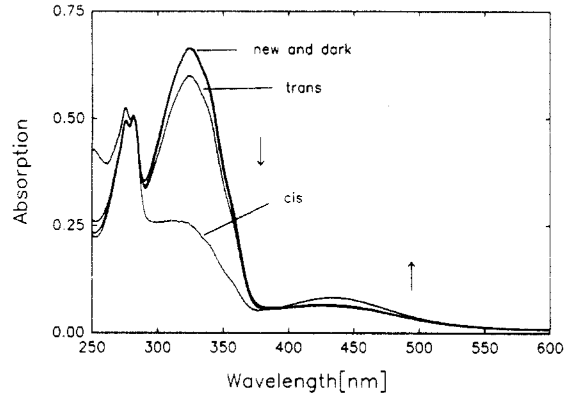
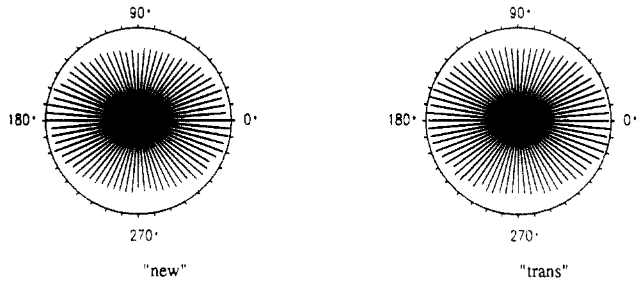


Figure 4. UV–vis spectra of a LB film of the copolymer (136 layers on quartz).

in Figure 3. In addition, UV–vis spectra of the film give information about the aggregation and orientation of the chromophores. The π–π^* band is shifted toward shorter wavelengths for parallel and toward longer wavelengths for antiparallel aggregation.[8,25,26]

The transition dipole moment of the π–π^* band is directed along the long axis of the azobenzene group.[25,27] Therefore the orientation of the chromophores in the LB film can be investigated by polarized UV–vis spectroscopy.

A comparison of the spectra in solution (Figure 3) and of a "new" LB film (Figure 4) shows neither a shift of the peak maximum nor a shoulder. Therefore it can be concluded that there is no aggregation of the chromophores in the LB film as has been found for polyglutamates with a higher content of azobenzene moieties.[20] The reason for this is the shielding of the chromophores by the alkyl groups of the (hexadecyloxy)benzyl moiety.



"new" "trans"

Figure 5. Absorption at the peak maximum (348 nm) depicted as vector against the angle between the plane of polarization of the incident light and the dipping direction.

As can be seen from Figure 5, the chromophores have a preferred orientation of approximately 0° with respect to the dipping direction. (The graph shows the normalized absorption at the peak maximum as vector versus the angle between the plane of polarization of the incident light and the dipping direction.) The orientational order in the xy plane is weak ($S_{348} = 0.09$). This preferred orientation might be caused by the side-chain conformation, which should be very similar to that found for poly(5-(4-phenylbenzyl) L-glutamate).[28]

Upon irradiation with UV light the π–π^* band diminishes and the n–π^* band increases due to the trans–cis isomerization. There are only minor differences between the spectra obtained from a solution and a "cis" LB film of the copolyglutamate as can be seen by comparison of Figures 3 and 4. The reason for this is that the chromophores in the LB films are in an environment very similar to a solution due to the alkyl groups of the (hexadecyloxy)benzyl moiety. Investigations concerning the aggregation and the orientation of the chromophores in the cis photostationary state by UV–vis spectroscopy are impossible due to the weakness of the π–π^* band of the trans isomer. The π–π^* band of the cis isomer is not suitable for evaluation because the transition dipole moment is not "uniaxial" and tilted approximately 40° with respect to that of the trans isomer.

Upon irradiation with visible light ($\lambda > 470$ nm) a trans-rich photostationary state is reached as shown in Figures 3 and 4. There are only minor differences between the spectra of the solution in the "trans" state and the "trans" LB film. The preferred orientation of the chromophores at 0° with respect to the dipping direction is retained upon irradiation ($S = 0.09$). Upon thermal back-isomerization to 100% trans, the original spectrum is restored (dark, Figure 4). The isomerization of the chromophores, therefore, is a fully reversible process with no reorientation, as has been found in the case of polyglutamates with a higher content of azobenzene moieties.[20]

X-ray Diffraction. The scattering curve for a "new" LB film of 22 layers of the copolyglutamate (Figure 6a) shows two important features, a modulation of the reflectivity, the so-called Kiessig fringes, and one Bragg peak (marked by an arrow). Both parts can be analyzed by modeling the electron density of the sample using the first Born appoximation to calculate the resulting reflectivity. This method to fit the reflectivity curves is described for example in ref 19. The electron density profile is described in this approximation by the formula

$$\rho(z) = \rho_f + 2\rho_1 \cos(2\pi z/p)$$

where ρ_f is the average electron density of the LB film and ρ_1 is the modulation of the electron density, caused by the periodic variation within the film, which has the periodicity p.

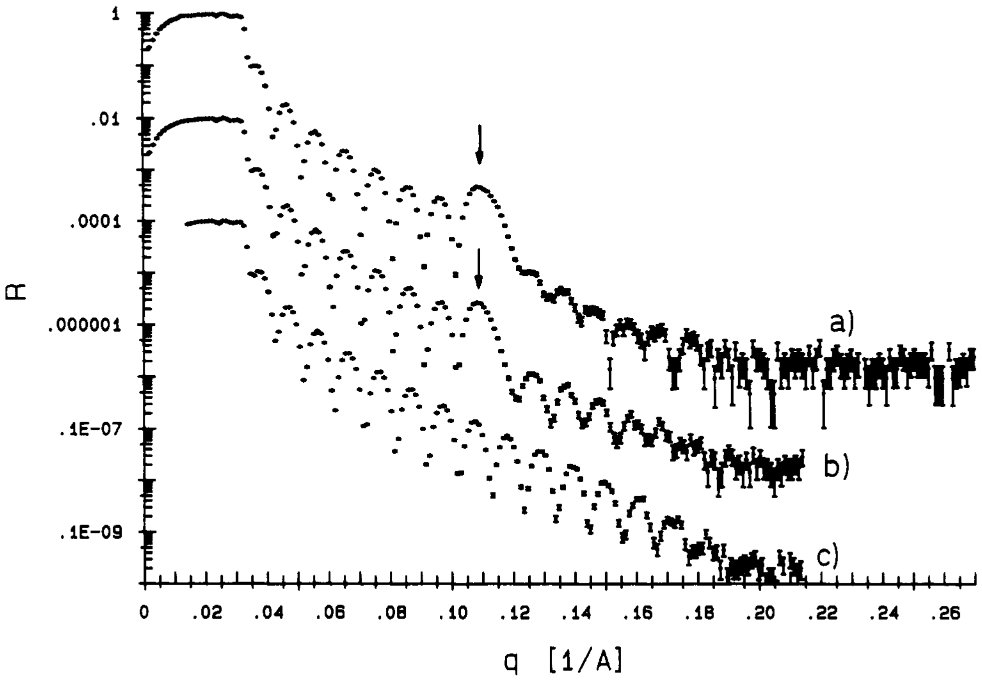


Figure 6. Reflectivity R of 22 layers of the copolyglutamate as a function of the momentum transfer q: (a) after preparation; (b) after 160 min of UV irradiation and 80 min of illumination with visible light; (c) reflection spectrum after 38 h at 90 °C.

Table II. Structural Parameters of 22 Layers of the Copolyglutamate on Float Glass

	treatment				
	as prepared	UV, 80 min	UV, 160 min	vis, 80 min	363 K, 38 h
total thickness (nm) ± 0.2 nm	60.6	60.5	60.4	60.4	60.0
surface roughness (nm) ± 0.1 nm	0.09	0.09	0.09	0.09	0.11
substrate roughness (nm) ± 0.1 nm	0.17	0.15	0.15	0.15	0.11
film electron density ($\times 10^{-3}$ nm^{-3}) ± 1.5 × 10^{-5} nm^{-3}	0.310	0.310	0.310	0.310	0.310
period (nm) ± 0.01 nm	5.65	5.65	5.65	5.65	
modulation of electron density ρ_1 ($\times 10^{-3}$ nm^{-3}) ± 1.5 × 10^{-6} nm^{-3}	0.012	0.010	0.008	0.006	0.000

The total thickness of the multilayer assembly causes the Kiessig fringes. Therefore the total thickness of the film can be determined by analyzing this part, mainly the periodicity of the modulation of the reflectivity. In the case of Figure 6a we get 60.6 ± 0.2 nm. The Bragg peak indicates a well-defined layered structure, because it is a result of the periodic structure of the LB film. This Bragg peak can be fitted with a periodicity of 5.65 ± 0.01 nm. Comparing the total thickness and the number of layers times the periodicity, we conclude that one bilayer forms a period. This Y-type transfer from the water subphase is also familiar from other polyglutamates.[20] The discrepancy between the number of bilayers times the periodicity and the total film thickness is an effect of the missing correlation between the first and last bilayer of the sample and the rest of the film. These layers near the substrate and the interface to the air do not belong to the periodic assembly, because they are not surrounded symmetrically by equivalent layers.

The surface and interface roughness is also available by this technique. Values with errors are shown in Table II.

After illumination with UV light, the total thickness periodicity is unchanged. Only the Bragg peak height is reduced due to a decreasing electron density modulation ρ_1. The same occurred with the use of visible light: only the Bragg intensity changes. After a total irradiation time of 240 min, the Bragg peak is clearly reduced (Figure 6b). Figure 7 shows that ρ_1 is linearly decreasing with an increasing duration of illumination. This indicates that the photon energy is being absorbed and dissipated as heat within the film. To clarify this point, we annealed the sample for 38 h at 367 K (a temperature quite above the 312 K melting temperature of the alkyl side chains[15]) in an evacuated oven. The tempered film shows no Bragg peak (Figure 6c), and the total thickness is approximately unchanged.

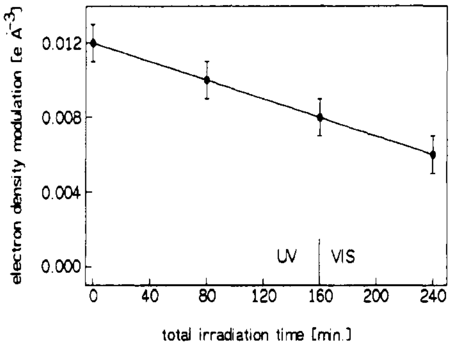


Figure 7. Electron density modulation ρ_1 of the LB film as a function of total irradiation time t. The curve can be fitted with the function $\rho_1(t)$ = 0.012 e/Å^3 × (1 − t/480 min).

Discussion

From the SAXS, FT-IR, and UV–vis data a preliminary model for the structure and the structural changes of the LB film can be deduced. The FT-IR spectra clearly show a preferred orientation of the main chains in the dipping direction. The SAXS data reveal a bilayered structure (Y-type LB film). Such bilayers could not be obtained from "hairy rods" with a symmetrical distribution of the side chains around the main chain; therefore deformed "hairy rods" with a more elliptical cross section are suggested (see Figure 8). The deformation is caused by the interaction of the hydrophobic side groups and the

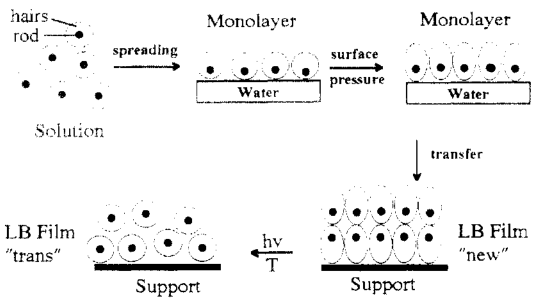


Figure 8. Schematic representation of the deformation process and the transfer of the "hairy rod" polymers.

more hydrophilic polyglutamate main chain with the water surface as well as by the compression of the monolayer due to the surface pressure on the trough.[20] This deformation is retained while transferring the monolayers to a LB multilayer assembly on a substrate.

The trans–cis and cis–trans photoisomerization processes proceed to a high extent, demonstrating a high molecular flexibility or sufficient free volume.[26,29–32] The chromophores are separated from each other by the alkyl chains; in this way aggregation of the azobensene moieties cannot take place. These two effects lead to a solution-like environment for the chromophores in the LB film.

Taking the above considerations into account, it is easy to understand why there are only minor changes in the scattering curve and, therefore, in the structure of the LB film when irradiated. The photoreaction changes the molecular form anisotropy and the dipole moment of the chromophore. In this way the mobility of the chromophore is enhanced. However, this does not alter the supramolecular structure in a specific and quickly photon mode driven sense. The photoreaction of the isolated azo moieties does not induce a cooperative process in the matrix of crystalline alkyl chains. However, on continued irradiation the increased local mobility induces a reorganization process toward the more stable symmetric distribution of the side chains around the main-chain helix. The same process can be observed when the LB film is heated above the melting temperature of the side chains (312 K[15]). In Figure 9 schematic of the microscopic model of this reorientation process is shown and compared with the electron density of the periodic structure after preparation.

The preferred orientation of the main-chain helices in the dipping direction remains unaffected by this process. Because the chromophore is located at the interface between the main-chain core and the shell of the alkyl chains,[28] this process also does not affect the spectral properties of the chromophore.

Conclusions

Relaxation of the metastable structure present in a "new" LB, which is characterized by bilayers composed of deformed "hairy rods", can be caused by irradiation. But it seems to be rather a slow thermal (or photochemical) induced reorganization than a fast photon-driven cooperative process. This relaxation affects neither the environment and orientation of the chromophores nor the orientational order of the main-chain helices in the *xy* plane. Therefore the optical properties of the entire film remain nearly unchanged, and the differences between irradiation and nonirradiated areas are too small to be detected by surface plasmon microscopy.

To get materials suitable for optical data storage, higher amounts of azobenzene chromophore in the LB film have to be realized. This can be accomplished either by synthesizing unipolymers with azobenzene derivatives equipped with alkyl groups as side chains[20,33] or by incorporation of a low molecular weight azobenzene derivative into the copolymer LB film. In the latter case the interaction of bound and unbound chromophore is used to stabilize the homogeneous distribution.

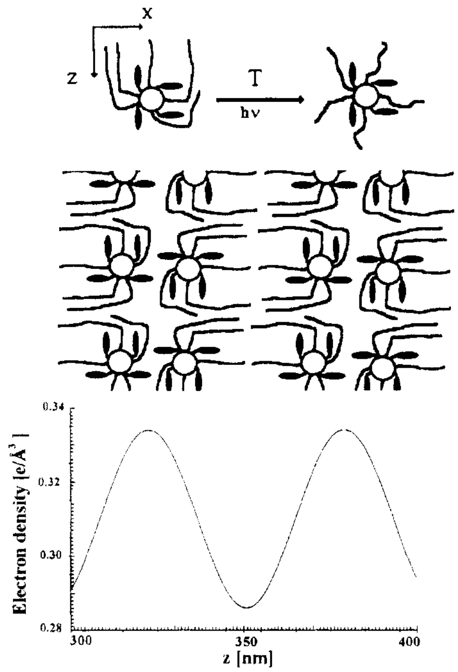


Figure 9. Electron density of two periodicities of the copolyglutamate compared with a model of the LB film. *z* is the distance from the glass/film interface.

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