Langmuir–Blodgett Films of Photochromic Polyglutamates. 5. Mixtures of a Photochromic Polyglutamate and a Low Molecular Weight Azo Dye

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ABSTRACT: In order to enhance the content of photoisomerizable chromophores in monolayers of the "hairy rod" like poly[5-(4-phenylazobenzyl) L-glutamate-*co*-5-[4-(hexadecyloxy)benzyl] L-glutamate], [4-(hexyloxy)phenyl]azobenzene was admixed. For the low molecular weight dye in the *E* form, miscibility was found up to a content of three dye molecules per polymeric chromophore, by recording *F*/*A* isotherms for different compositions. The influence of the dye is more pronounced in the case of the polymeric chromophore in the *E* form, suggesting interactions between the different azobenzene moieties. The monolayers can be transferred to Langmuir–Blodgett (LB) films. The UV–vis spectroscopic results on these films also reveal enhanced interactions if both mixing partners are in the *E* form. Furthermore, structural changes upon irradiation could be detected within the LB films. Despite the interactions between the azobenzene moieties, there are segregation phenomena impeding the use of the mixed LB films in optoelectronical applications.

Introduction

Polymers with a rigid-rod-like backbone and flexible side chains, so-called "hairy rods", are capable of forming stable monomolecular films at an air/water interface. The monolayers can be transferred to substrates using the Langmuir–Blodgett (LB) technique. The resulting LB films are homogeneous and stable and exhibit unique properties.[1] Poly[5-(4-phenylazobenzyl) L-glutamate-*co*-5-[4-(hexadecyloxy)benzyl] L-glutamate] (1) was synthesized in order to obtain a polymer with properties to be altered by the photochemical isomerization of the photochromic azobenzene moiety.[2] This polymer gives high-quality LB films, and the isomerization of the azobenzene moieties proceeds to a high extent upon irradiation with UV light. However, there are only minor structural changes within the LB film, which are too small to be detected by surface plasmon microscopy.[2] This is attributed to the flexibility of the alkyl side chains, which are capable of compensating the motions occurring during the photoisomerization[2,3] and the low content of chromophores (16%) in the copolymer. The content can be enhanced either by substitution of the alkyl chains with an alkyl-substituted azobenzene derivative[4,5] or by incorporation of a low molecular weight dye. In the latter case migration and segregation of the admixed dye might be a problem. Therefore, interactions between the admixed dye and the chromophore tethered to the polymer backbone are required. Such interactions can be expected if azobenzene chromophores are used because of their strong tendency to aggregate.[6-9] It is known that the azobenzene chromophores aggregate in ordered systems like micelles and vesicles,[6] liquid crystalline phases,[8,10] or LB films[7,9] if the order is sufficient and if the distance between the chromophores is not too big. Within the aggregates the chromophores can be arranged in a parallel or antiparallel manner, which results in different absorption spectra.[11] This aggregation tendency is lost when the chromophores are isomerized to the *Z* form,[10] because of the loss of the elongated shape of the molecule. This paper will report on the miscibility of the copolymer, either in the *E* form (1) or in the *Z* form (2), and the low molecular azobenzene dye (*E*)- (3) and (*Z*)-[4-(hexyloxy)phenyl]azobenzene (4) in monolayers. Furthermore, spectroscopic studies were carried out on the LB films obtained by transferring mixed monolayers (3/1 and 3/2) to substrates. Because of the shift of the $\pi-\pi^*$ band upon aggregation[11] and orientation of their transition dipole moment along the long axis of the azobenzene chromophore,[6] the UV–vis spectroscopy is well suited for structural investigations.

Experimental Section

Materials. The investigations were carried out with poly[5-(4-phenylazobenzyl) L-glutamate-*co*-5-[4-(hexadecyloxy)benzyl] L-glutamate] (1) with 16 mol % of the azobenzene moieties. Synthesis, characterization, and spreading behavior of the polymer were described earlier.[2] [4-(Hexyloxy)phenyl]azobenzene (3) was used as low molecular weight dye. To examine the influence of the isomerization on the miscibility and the structure of the LB film, solutions with different contents of *E* isomer were spread onto the water surface. 100% *E* isomer can be obtained by storing the solutions for 7 days at ambient temperature in the dark. By irradiation with UV light, 93% of the chromophores in the copolymer (2) and 88% in the case of the low molecular weight dye can be isomerized to the *Z* form (4).[2]

Quartz slides (Hellma, Suprasil fused silica optical windows) 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. Irradiations were carried out using a 200-W high-pressure mercury lamp (Oriel) employing a cut-off 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 IR radiation. The light impacted perpendicular on the LB film. For experiments tracing the *E*–*Z* isomerization by UV–vis spectroscopy, a less intense immersion lamp (Philips HPK125) was used, employing a band-pass filter to obtain light with a wavelength $\lambda = 360 \pm 50$ nm (DEMA UVW-55). A water filter was used to remove IR radiation. In this case the light was diffuse.

The polymers were spread from chloroform solutions on a Lauda FW 1 trough filled with ultrapure water (>18 MΩ·cm; Barnsteadt NanoPure III) at 20 °C. After a period of at least 15 min the isotherm was recorded or the film was compressed to the intended surface pressure (25 mN/m), using a Langmuir

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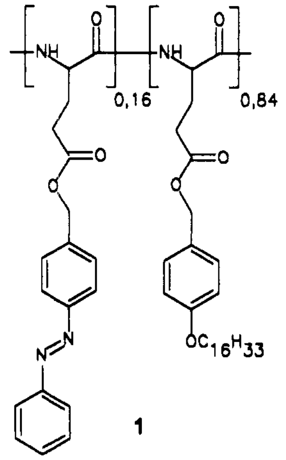

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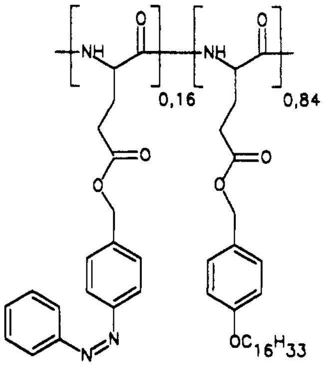

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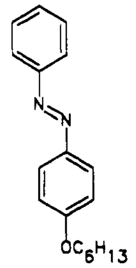

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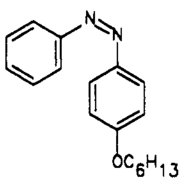

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balance for surface pressure registration. After the surface area had stabilized at this pressure, the transfer was started using a Lauda FL-1E filmlift. The substrate was oriented parallel to the barrier. The dipping rate was adjusted to 25 mm/min. The transfer ratios were determined from the decrease in surface area. The area per monomeric unit is determined as the area at the point of collapse A_k.

A LB film is called "new" when a solution is spread to a monolayer and this monolayer is transferred to a LB film under red light conditions to prevent photoisomerization. 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).

UV–vis spectra were recorded on a Perkin-Elmer Lambda 5 instrument.[12] Polarization was performed using a Glan–Taylor prism polarizer from calcite (LOT). For the polarization labeled $\|$, 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 ($E \| x$; see Figure 1). The polarization labeled $\perp$ is rotated by 90° from this direction ($E \| y$; see Figure 1).

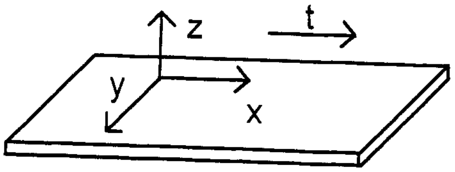

Figure 1. Geometrical relations. t = dipping direction.

The order parameters were calculated by $S = (A_\| - A_\perp)/(A_\| + 2A_\perp)$ ($A_\|$ = absorption in the preferred direction, $A_\perp$ = absorption at 90° to the preferred direction).

Results and Discussion

Miscibility. In order to examine the miscibility, solutions of the copolymer and the low molecular chromophore in the different states of isomerization were mixed in different ratios. These mixtures were spread at the air/water interface and the surface pressure (F)/surface area (A) isotherms were recorded at 20 °C. The surface area was recorded as the area per monomeric unit of the copolymer. This kind of plot is favorable, because it shows whether the low molecular weight dye, which does not form a stable monolayer itself, alters the monolayer of the copolymer.

Both Mixing Partners as *E* Isomer. The F/A isotherms for the mixtures of **3** in **1** are depicted in Figure 2. In this case both the dye and the polymeric chromophores are in the E form. If the ratio **3**/chromophores in **1** does not exceed 3:1, there is no drastic change in the isotherm, but there is a gradual increase of the area per monomeric unit at the collapse point. Concomitantly the surface pressure at the collapse point (see Figure 3) decreases. This result is an indication for complete miscibility of the dye in the monolayer of the copolymer.[13,14]

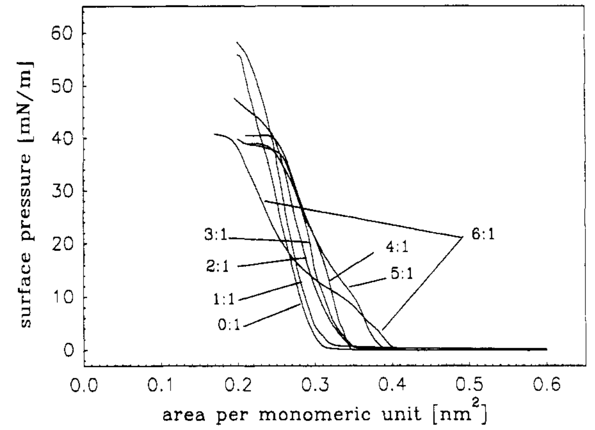

Figure 2. Surface pressure/surface area isotherms of mixtures of **3** and **1** (dark adapted solutions; both chromophores E isomers).

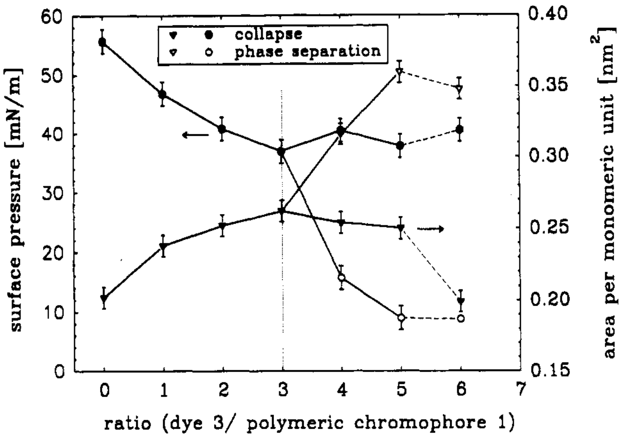

Figure 3. Surface area (circles) and surface pressure (triangles) at the point of collapse (filled symbols) and at the point of phase separation (hollow symbols) for monolayers of mixtures of **3** and **1**.

If the ratio **3**/chromophores in **1** exceeds 3:1, an additional step in the isotherm occurs, which can be ascribed to a segregational phenomenon, because the isotherm at pressures above this step is equal to that obtained from a mixture with a ratio of 3:1. There are no further changes in the surface area per monomeric unit and the surface pressure at the point of collapse. The corresponding curves in Figure 3 nearly exhibit a plateau. At very high amounts of low molecular weight dye (**3**/chromophores in **1** > 5:1) no stable monolayer is formed

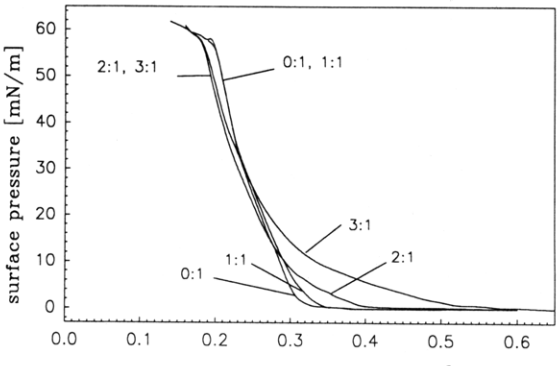

Figure 4. Surface pressure/surface area isotherms of mixtures of **2** and **4** in various ratios.

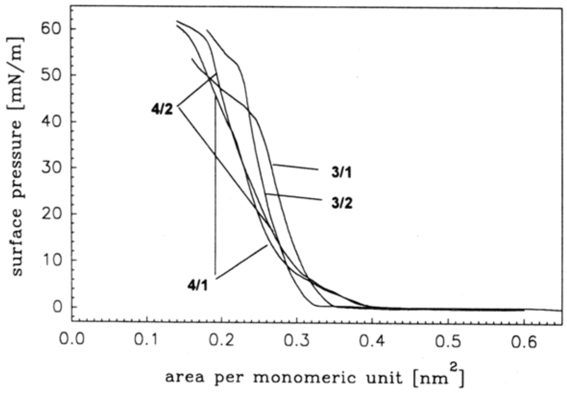

Figure 5. Comparison of the isotherms for mixtures with mixing partners in different isomerization states (mixing ratio 2:1 (low molecular dye/polymeric chromophore)).

or the excess of low molecular weight dye acts as a plastifier.[15]

Both Mixing Partners as *Z* Isomer. If both the low molecular weight dye and the polymeric chromophores are in the *Z* form (**4** and **2**), the situation is different. The surface area at which the first surface pressure occurs is increased even at very low ratios **4**/chromophores in **2**. The slope of the isotherm is small. At higher surface pressures the isotherms resemble that of the pure copolymer. Furthermore, the surface pressures at the collapse point for the different mixtures are very similar (see Figure 4). This is an indication that the dye is rejected from the monolayer at low surface pressures and therefore an indication that the mixture of **4** in monolayers of **1** is not a stable one, even at very low dye content. This can be understood by taking into account that in this case there is no interaction between the different azobenzene moieties, which are in the *Z* form. Furthermore, the (*Z*)-azobenzene moiety is bended and polar, and therefore interactions with the alkyl chains are hindered, but interactions with the water surface are possible. Only the hexyl moiety can interact with the side chains of the polymer, resulting in a weak interaction.

Mixing Partners in Different Isomerization States. If the mixing partners are in different isomerization states, the resulting isotherms lie in between the results obtained with mixtures of the partners both in the same isomerization state. In Figure 5 the isotherms of the mixtures with a ratio of 2:1 (dye/polymeric chromophore) are compared. As in the case of mixtures of **4**/**2** the form of the isotherms and the surface pressure at the collapse point indicates that mixtures of **4**/**1** are not stable and the dye is rejected from the monolayer.

The situation is different if the dye is admixed as *E* isomer (**3**) to the monolayer of the copolymer with the chromophore as *Z* isomer (**2**). In this case the isotherms show one steep rise and the area at the collapse point has increased compared to the monolayer of the pure copolymer. However, compared to the previously described case with the polymeric chromophores in the *E* form (**1**), the increase in the collapse area is small. In this case there are no interactions between the polymeric chromophores, which are in the *Z* form, and the low molecular weight dye molecules. For this one can suppose that the dye is located in the region of the alkyl side chains, stabilized by the hydrophobic interactions between the alkyl chains and the dye. The dye molecules are very mobile within the side-chain region and do not hinder the deformation of the hairy rod molecules, which occurs when the hairy rods are exposed to the surface pressure at the air/water interface[3,5] (see Figure 6), and therefore do not increase the area significantly. If the polymeric chromophores are also in the *E* form (**1**), there are, in addition to the hydrophobic interactions, interactions between the chromophores and the dye molecules. The dye molecules are located near the main-chain helix and are not as mobile as in the case described before. Therefore, the deformation of the hairy rod is hindered and the area per monomeric unit is increased.

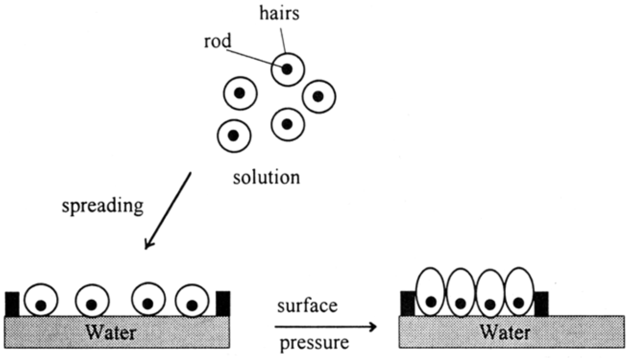

Figure 6. Schematic representation of the deformation of the hairy rods upon spreading and compression.[3,5]

LB Films. If the dye is admixed as *E* isomer and its content does not exceed a ratio of 2:1 (dye/polymeric chromophore), the mixed monolayers are stable enough to be transferred to substrates by means of the Langmuir–Blodgett technique. The transfer rate was determined to 95 ± 3%.

The absorption of the (*E*)-azobenzene moiety is characterized by the π–π^* band in the region of 330 nm and the n–π^* transition at 440 nm. In addition, in the spectrum of the copolymer there are bands from the benzyl moiety at 245 and 265 nm. The π–π^* band is shifted and diminished upon *E*–*Z* isomerization. Using polarized light for UV–vis spectroscopy, the orientation of the chromophores within the *xy* plane (see Figure 1) can be investigated because the transition dipole moment of the π–π^* band is directed along the long axis of the chromophore.[6,16]

The UV–vis spectrum of a LB film of a mixture of **3** and **1** (ratio 1:1) shows a "normal" peak for the π–π^* absorption band of the chromophore. This peak can be considered as a combination of the peak of the dye and the polymeric chromophore (see Figure 7). In solution the sum of the spectra of the components is identical with the spectra obtained from a 1:1 mixture. The UV spectrum of the corresponding LB film is slightly different. The absorption is strongly enhanced for the bands related to the benzyl moiety at 245 and 265 nm. This enhanced absorption is also found for LB films of pure copolymer **1** and is a result of the preferred orientation of the chromophores and

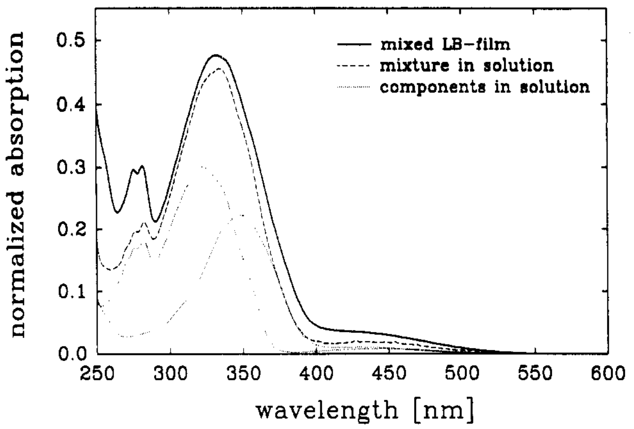

Figure 7. UV–vis spectra of a LB film (120 layers) and a solution of the mixture **3**/chromophores in **1** (1:1) and of the components in solution (absorption normalized to 10^{16} azobenzene moieties/cm^2 or 10^{16} azobenzene moieties/cm^3 in a 1-cm cell, respectively).

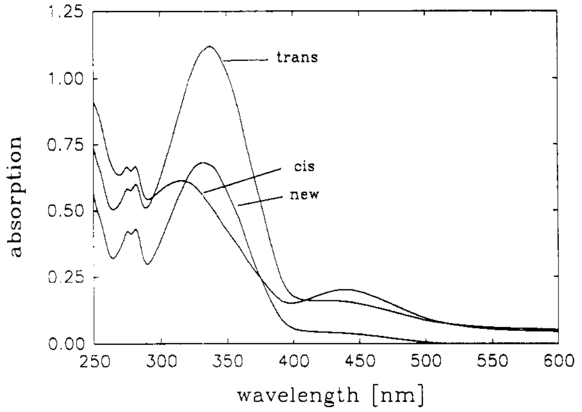

Figure 8. UV–vis spectra of a LB film of the mixture **1**/**3** (1:1): new = freshly prepared; cis = irradiated with UV light until the cis photostationary state is reached; trans = irradiated with visible light until the trans photostationary state is reached.

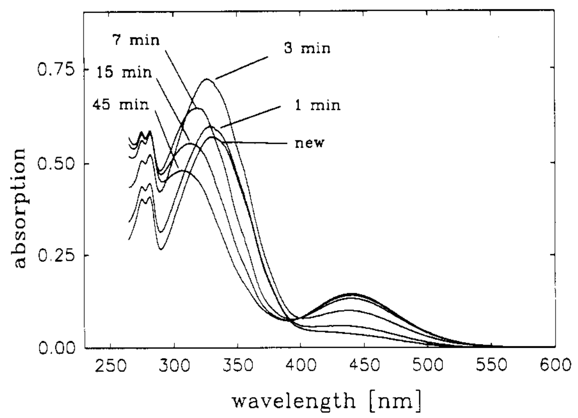

Figure 9. UV–vis spectra of a LB film of the mixture **1**/**3** (1:2), recorded after different irradiation times (less intense lamp) and with different amounts of Z isomer.

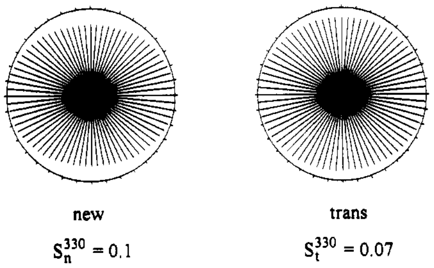

Figure 10. Absorption at the peak maximum (330 nm) depicted as a vector versus the angle between the plane of polarization of incident light and the dipping direction for the freshly prepared LB film (new) and the LB film after irradiation with UV and visible light.

benzyl moieties in the xy plane.[17] The preferred orientation is caused by the conformation of the side chains with respect to the main-chain helix[18] and the orientation of the helices due to the flow effects in the transfer process.[19] In the case of the LB film of the mixture, the absorption for the π–π^* band of the chromophores (polymeric chromophores, which are lying preferentially in the xy plane, and low molecular weight dye) is only slightly enhanced compared to the solution. From this it can be concluded that the low molecular weight dye is partly oriented in the z direction. The chromophores lying in z direction are "invisible" for the spectrometer, and the absorption in the spectrum is smaller than expected. This effect should be accompanied by a shift of the peak maximum, because the mixing partners have different spectra with peak maxima at different wavelengths. Such a shift of the peak maximum is not observed, because it is superimposed by the peak shift due to aggregation of the chromophores.[11,20,21]

The partial z orientation of the dye molecules in the freshly prepared LB film can be destroyed by irradiating the film with UV light. Upon irradiation E–Z isomerization of the dye molecules and the polymeric chromophores takes place, as can be seen in the UV–vis spectra by the decreasing π–π^* band (see Figure 8). Using visible light the azobenzene moiety can be reisomerized to some extent (trans photostationary state in solution about 90% E isomer). In the spectra of the LB film of the mixture in the E photostationary state, the π–π^* band absorption is stronger than in the freshly prepared film, although there are less chromophores in the E form. Therefore, some reorientations must have taken place in the LB film, enhancing the number of chromophores accessible for the spectrometer. Such reorientations have also been observed in the case of unipolymers with azobenzene moieties tethered by a spacer.[5] In the case of higher dye content (1:2) the z orientation is more pronounced and the reorientation can be ascertained by recording UV–vis spectra while isomerizing the azobenzene moieties. In Figure 9 the spectra recorded after different irradiation times with UV light (with different amounts of Z isomer[2]) are depicted. A gradual decrease of the absorption in the region of the π–π^* band was expected, but after short irradiation times (1 min, ca. 50–60% Z isomer[2]) the absorption is higher than that of the freshly prepared film. Upon further irradiation there is the expected gradual decrease. This suggests that the reorientation takes place after short irradiation times and that there are photochemically induced structural changes in the mixed LB films which could not be detected in LB films of the pure copolymer.[3]

The polarized spectroscopy reveals that the chromophores (or rather their projection into the xy plane) are preferentially oriented in the x direction within the the xy plane. Figure 10 shows the normalized absorption at the peak maximum as a vector versus the angle between the plane of polarization of the incident light and the dipping direction. The orientational order is weak. The order parameters are calculated as $S_n^{330} = 0.1 \pm 0.025$ and $S_t^{330} = 0.07 \pm 0.025$.[22] These values are in the range found for the copolymer LB films[3] and can be attributed to the side-chain conformation, which should be very similar to that found by Sisido et al.[18] and the orientation of the main-chain helix due to the flow effects in the transfer process.[19] The order parameter decreases if the dye content increases ($S_n^{330} = 0.06 \pm 0.025$ and $S_t^{330} = 0.04 \pm$

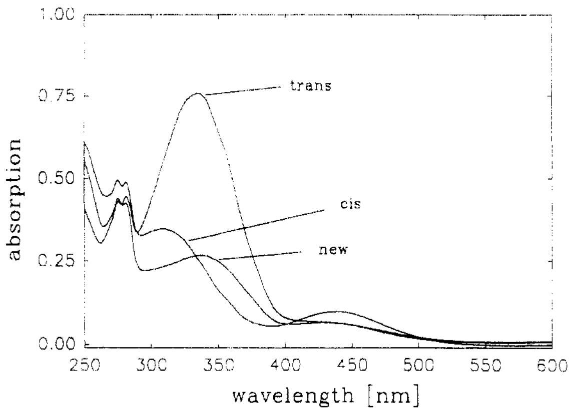

Figure 11. UV–vis spectra of a LB film of the mixture 3/chromophores in 2 (1:1): new = freshly prepared; cis = irradiated with UV light until the cis photostationary state is reached; trans = irradiated with visible light until the trans photostationary state is reached.

0.025[22] for the 1:2 mixed LB film), indicating the higher mobility of the low molecular weight dye.

The UV spectrum of a LB film of a mixture of **3** and **2** (ratio 1:1) shows only a very small absorption in the region of the π–π^* band (Figure 11). This can be explained by taking into account that the polymeric chromophores are in the *Z* form and do not absorb significantly in the π–π^* band region and that the low molecular weight dye **3** is very mobile because there is no interaction with the polymeric chromophore. Because of this lack of interaction, the dye molecules are located in the alkyl chain region and are preferentially oriented in the *z* direction due to the deformation of the hairy rod (see Figure 6).[3] This orientation is destroyed upon irradiation, and the absorption of the film in the photostationary state "trans" is higher than the absorption of the freshly prepared film.

A further interesting feature is the absorption at wavelengths larger than 500 nm occurring in the spectra of the irradiated LB films (see Figure 8). This unspecific absorption can be attributed to the scattering due to crystallites and is therefore an indication for segregation. The low molecular weight dye segregates upon irradiation because the polar (*Z*)-azobenzene does not interact with the alkyl tails of the polymer as the (*E*)-azobenzene does. If the LB film is stored in the dark, this scattering increases because the crystallites grow. After 2 weeks small crystals of **3** can be seen on the LB film using a polarization microscope. The crystals are up to 20 μm in diameter. The crystal size is a function of several parameters (such as the number of irradiation cycles, duration of storage in the dark, temperature, etc.) and therefore not reproducible.

Conclusions

The *F*/*A* isotherms of the different mixtures of the copolymer and the low molecular weight dye reveal that the dye in the *Z* form (**4**) is rejected from the monolayer. However, the dye in the *E* form (**3**) is miscible with the copolymer, as well as with the polymeric chromophore in the *E* form (**1**) and in the *Z* form (**2**). In both cases the miscibility is limited to a ratio of approximately 3:1 (dye/polymeric chromophores). When both the dye and the polymeric chromophores are in the *E* form, there is an interaction between the azobenzene moieties in addition to the hydrophobic interactions. Due to this additional interaction, the dye is preferentially located in the vicinity of the main-chain helix, resulting in an increased area per monomeric unit because the deformation of the hairy rod is hindered.

The mixed monolayer, in which the ratio of dye to polymeric chromophore does not exceed 2:1, can be transferred to LB films. From the UV–vis spectroscopic data it can be concluded that the low molecular weight dye is oriented normal to the substrate to some extent. This *z* orientation is more pronounced in the case of the copolymer in the *Z* form. Because of the lack of interactions between the dye and the polymeric chromophores, the dye is more mobile within the monolayer and preferentially located in the side-chain region, which is deformed in the *z* direction due to the surface pressure.

With an irradiation cycle (irradiation with UV light, which causes *E*–*Z* isomerization, and subsequent irradiation with visible light, which causes *Z*–*E* isomerization) some reorientations within the LB film can be induced. Because of this the mixed LB films seem to be suited for use in a setup for optical data storage. But after an irradiation cycle segregation phenomena, such as light scattering and crystals on the LB film, occurred. So the homogeneity of the LB films, which is a prerequisite for optoelectronical applications, is no longer present. The occurrence of the segregation reveals that the interactions between the dye and the polymeric chromophores, especially as *Z* isomers, are not sufficient. Therefore, to obtain materials suitable for electroptical applications, the dye content has to be enhanced by substitution of the alkyl chains in the copolymer by azobenzene moieties equipped with alkyl chains, rather than by admixing a dye.

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