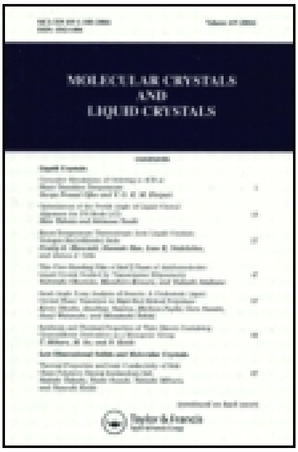

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Photochemically Induced Changes of Optical Anisotropy and Surface of LB-Multilayers Built up by an Amphiphilic and Liquid Crystalline Copolymer Containing Azobenzene Moieties

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PHOTOCHEMICALLY INDUCED CHANGES OF OPTICAL ANISOTROPY AND SURFACE OF LB-MULTILAYERS BUILT UP BY AN AMPHIPHILIC AND LIQUID CRYSTALLINE COPOLYMER CONTAINING AZOBENZENE MOIETIES

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Abstract: Amphotropic copolymers containing rod-like side groups combine the ability to form Langmuir-Blodgett multilayer assemblies with thermotropic liquid crystalline selforganization on temperature changes. Photochromic azobenzene side groups affect the supramolecular structure in such copolymers in dependence on irradiation wavelength and polarization of the incident light beam as well as temperature. The aggregation phenomena at the polymer air interface caused by the amphotropic properties of the material were reversibly modified by the light induced variation of the molecular shape of the photochromic moieties. The vertically layered structure had been destroyed and rebuilt upon irradiation and annealing the LB films. Moreover, the optical in-plane anisotropy was erased on irradiation and reinduced using linearly polarized light.

Combined investigations (angular dependent UV-VIS measurements, energy dispersive SAXS and GID, high resolution AFM) provide new insights into the micromorphology as well as the surface structure of the condensed initial and transformed LB films.

Introduction

Langmuir-Blodgett multilayer assemblies of photochromic copolymers with rod-like azobenzene moieties as side groups show interesting changes of the supramolecular structure on annealing[1] and on irradiation[2] causing a variation of optical properties.

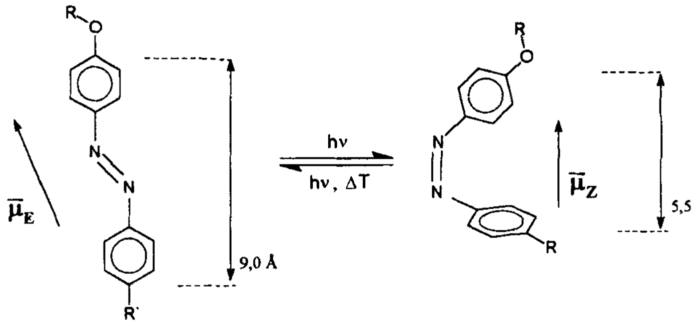

FIGURE 1 Photoisomerization of azobenzene derivatives

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Upon irradiation the azobenzene moieties undergo cis-trans photoisomerization changing the geometrical shape, dipole moment and the direction of transition moment of excitation (Figure 1). A steady state between rod-like trans isomers and the globular cis isomers is established in dependence on the excitation wavelength.

In LB films these changes affect the periodicity of lamellar layers and the overall thickness. Moreover, a sufficient disturbance usually led to a total and irreversible loss of the ordered structure within the films. However, in case of amphotropic polymers there is an additional possibility to induce reversibly a lamellar order in the system. Such polymers combine the ability to form LB multilayers due to the amphiphilic properties as well as liquid crystalline order by thermotropic selforganization.

Thus, changes in the structure of LB multilayers of amphotropic copolymers were studied in dependence on temperature[1]. Depending upon the preparation procedure and the treatment of the LB samples we subdivided[3] the states of surface aggregates and lamellar structures into several types which are (with the exception of the original LB state) capable of being reversibly transformed into each other by means of irradiation and thermal procedures. Reversible and irreversible changes of refractive indices in photochromic LB systems were recently demonstrated[4-6].

The modification of orientation and order by means of linearly polarized light was recently investigated in LB multilayers[7-13], films of amorphous[13-18] as well as liquid crystalline polymers[13,19-22]. The use of azobenzene surfaces for the photochemical control of liquid crystal alignment causing efficient and reversible variation of refractive indices in liquid crystal displays were successfully shown[23-27]. The reversible control of homeotropic and planar alignment of nematic liquid crystals by azobenzene containing ultrathin systems as „command surfaces“ was demonstrated upon illumination with UV and VIS light. Moreover, the orientational direction of the liquid crystals was modified upon exposure of such layers with linearly polarized light. These effects caused by the light-induced modification of the photochromic surface are not yet finally understood.

The structure and molecular aggregation phenomena at the polymer-air-interface of LB multilayer assemblies have been studied in dependence on light exposure (UV and VIS light respectively) by means of combined Atomic Force Microscopy investigations[28], polarized UV-VIS spectroscopy as well as by time resolved energy dispersive SAXS and GID measurements[29].

Experimental

Photochromic Langmuir-Blodgett multilayers of polymer 1 (Figure 2) were prepared by means of the Langmuir-Blodgett-Kuhn technique[30] (Figure 3). The amphiphilic copolymer exhibits liquid crystalline behaviour in bulk (g 30 k 56 s 86 i)[1].

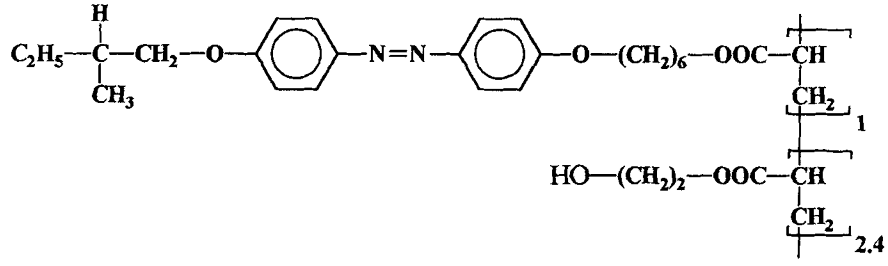

FIGURE 2 Amphotropic copolymer 1 with azobenzene side groups

Stable monolayers were obtained at 20.7°C in a KSV 5000 trough on pure water (Milli-Q-system) by spreading a 10^{-3} M $CHCl_3$ solution and extremely slow compression at about $5cm^2/min$. Surface pressure reading was performed with a Wilhelmy plate.

Transfer of the monolayers onto hydrophobic quartz plates was carried out with a dipping speed of 5 mm/min at a surface pressure of π_0 = 36 mN/m. Transfer ratios were on the down-stroke as well as on the up-stroke > 0.94. To keep the dark adapted material in the trans configuration care was taken by working in the absence of actinic light. Polarized UV-VIS spectra were measured on a Perkin-Elmer Lambda 19 spectrometer containing a self-designed construction kit to perform a 360 degree angle scan. The minimum and maximum absorbance yield the dichroitic ratio by $R= A_{max}/A_{min}$. Analogous to the method known from nematic liquid crystals a spectroscopic degree of order $S_{XY}=(R-1)/(R+2)$ was calculated to characterize the orientation. Irradiations were carried out by a mercury HBO 500 lamp and appropriate filters on a conventional optical desk as well as by an Inova 90 Ar^+ laser system (Coherent) at 357, 457.4 and 488 nm.

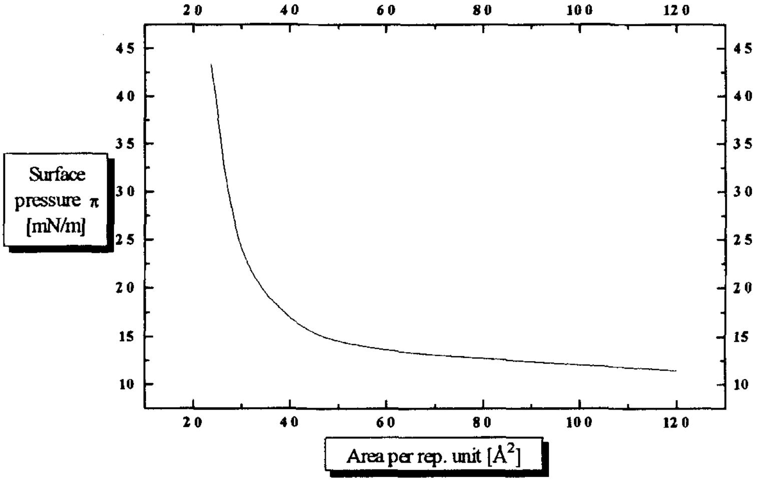

FIGURE 3 π-A-Isotherm of photochromic copolymer 1 at 20°C

Angular-dependent SAXS were carried out on a STOE Θ-Θ-refractometer; the energy dispersive SAXS were performed at a self designed instrument[31] using a Si(Li) detector and a multichannel analyzer (Silena). The resolution amounts to $\Delta d/d=2\%$. The change of lattice parameters under illumination with a HBO 100 lamp was observed in-situ with a time resolution of up to five minutes. Grazing incidence X-ray diffraction[32] (GID) was performed at D4 beam line (Hasylab) in order to evaluate the in-plane lattice parameter.

AFM micrographs were obtained with a Digital Instruments NanoScope II at room temperature with a microscopically selected and non-scraping[33] microfabricated Si_3N_4 cantilever (force constant 0.1 Nm^{-1}). 0.01 to 10 µm images were obtained under constant height and, in case of molecular resolution images, constant force mode conditions with a net tip force in the region of 1 to 10 nN. The planefitted three-dimensional micrographs at a pitch angle of 30° were processed with NanoScope III software by mixing illumination and height coding for best appearance. Flattening facilities were used throughout, median and low-pass filtering only sparingly to remove statistical noise for improving the glossiness of the pictures. This was done without loss of information.

Results

Initial LB films

An AFM-scanning micrograph of an original 64 layer LB-film with 46±1Å double layer spacing and the angular dependent absorbance at 335 nm depicted as vector length vs. the angle between the plane of polarization of incident light beam and the dipping direction (0-180°) are shown in Figure 4 monitored as a polar plot.

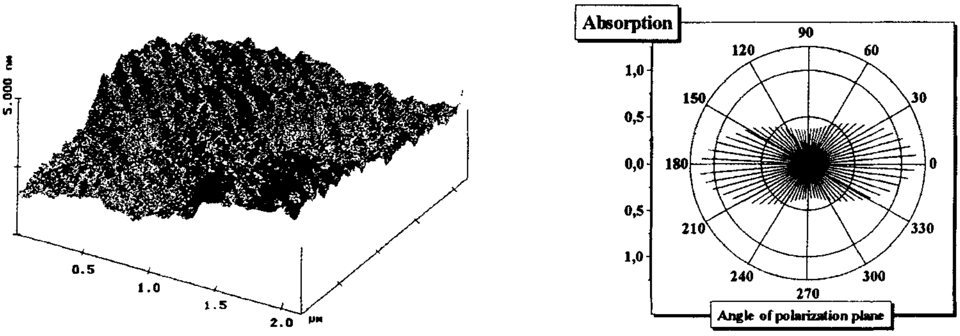

FIGURE 4 AFM micrograph of an original LB layer of polymer 1 with 64 layers scanned 45° to the dipping direction and angular dependent absorption at 335 nm

The stripes on the image are parallel to the dipping direction due to shear forces during the transfer process. The in-plane order parameter S_{XY} was 0.42 for a 64 layer film and in case of a 144 layer film it amounts to 0.512 (Figure 5). The various absorption behaviour of different aggregates is clearly seen in the angular dependent UV-VIS spectra. The dimeric chromophore absorption at 335 nm differs from that at 365 nm for monomers. The absorption band at about 385 nm is due to J-like aggregates[34].

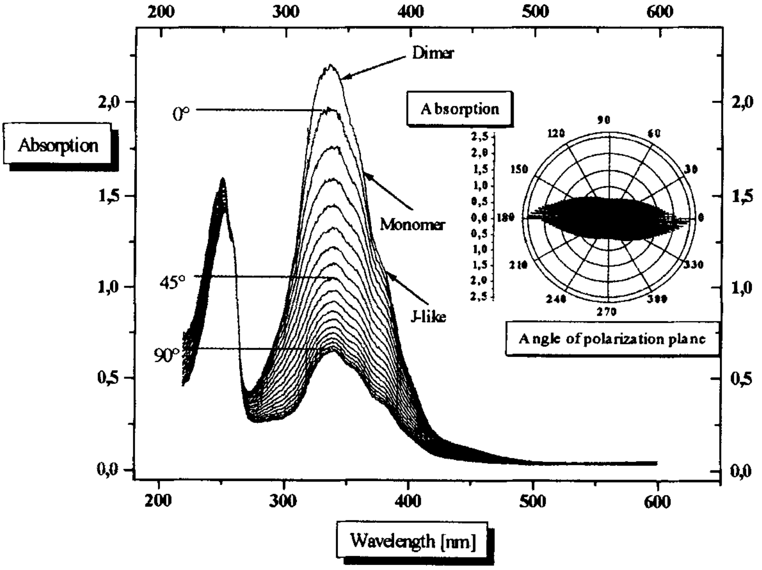

FIGURE 5 Angular dependent absorption spectra and polar plotted values at 335 nm for an initial 144 layer LB film of polymer 1

The angular dependent UV-VIS absorbance of the side groups in dipping direction (0-180° normalized) at 335 nm shown as polar plot indicates that the initial optical in-plane anisotropy was tilted by 8-15° to the layer normal in dipping direction inclined during the transfer process. In contrast to that the AFM image shows regularly folded stripes of the hydrophobic side groups due to the constrained polymer backbones. The average height amounts to 1.125 nm while the mean roughness is 0.659 nm. The results correspond to a tilted, close-packed and highly ordered double layer structure.

„Annealed" films

The phase transition from the constrained LB film into a new layered structure can be easily reached upon annealing at a temperature where the bulk polymer performs a smectic liquid crystalline phase. This observation was detected using time resolved SAXS. Only the first order Bragg peak could be monitored which corresponds to d=46Å for the LB film. Thermal fading of the first order Bragg-peak upon annealing of an original LB film with 64 layers at 63°C is shown in Figure 6 (graph B). After five minutes a X-ray amorphous state was established. Leaving the sample at 63°C (D) for 90 minutes a new layered structure was obtained with a double layer spacing of about 52±1Å due to the newly established liquid crystalline order in the film.

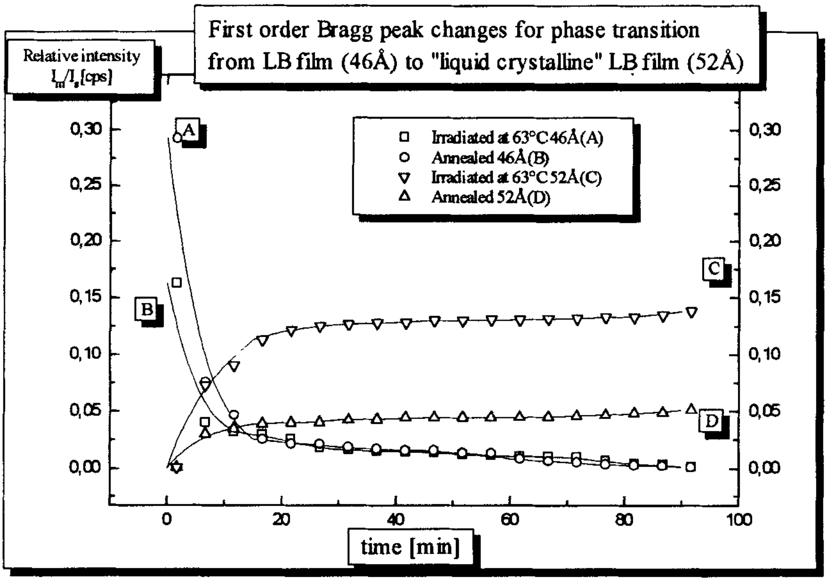

FIGURE 6 Light induced decay of the first order Bragg peak at 46Å upon irradiation with polarized light at 436 nm, 63°C (A) and on annealing without light incidence (B) as well as the light induced increase of the corresponding first order Bragg peak at 52Å upon irradiation with polarized light at 436 nm, 63.7°C and on annealing without light incidence (D)

This phase transition proceeds much more efficiently under the influence of linearly polarized light at 436 nm (A and C). Obviously, the disturbance of order and modified dynamics within the established steady state provoke the formation of a smectic-like double layer phase within the LB films.

After the phase transition the individual side chains are no longer tilted almost into the dipping direction. The end groups are now interdigitated into each other performing a double layer spacing which is larger than that in the constrained LB film. The initial LB structure can be annihilated at temperatures higher than 54°C. Once established the initial LB layer structure with the characteristic double layer spacing of 46Å can never be obtained back[8,9,30]. Performing the phase transition from the tilted to the stretched lamellar bilayer results in the erasing of the initial in-plane anisotropy (Figure 7).

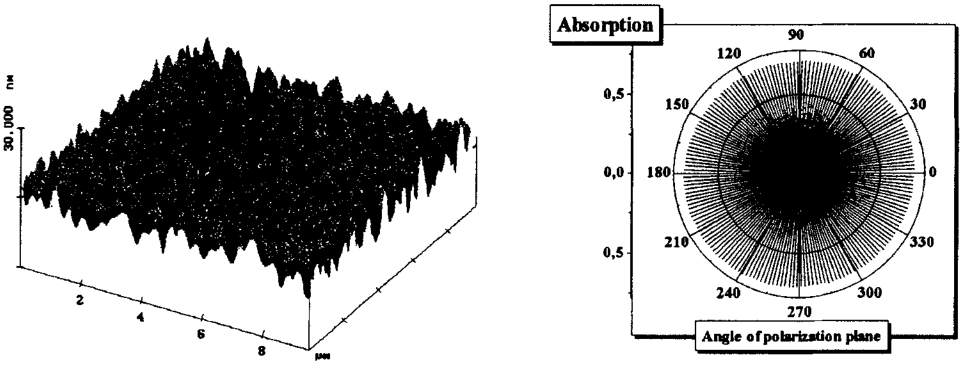

FIGURE 7 AFM image of an „annealed“ film after phase transition into the LC film and angular dependent absorbance at 335 nm for a 64 layer LB film (S_{XY} = 0.001)

The most characteristic AFM feature of the „annealed“ films is the appearance of regular platelets or clusters at the polymer air interface. Values for the average peak height and mean roughness were 6.25 nm and 3.15 nm respectively. This observation points to an irregular formation of individual domains in the LC state. The interpretation is supported by the appearance of further Bragg peaks with larger layer spacings of 55Å and 61Å in SAXS beside the above mentioned one. No relation to the former dipping direction can be observed under the conditions of the AFM image anymore.

Unpolarized UV irradiation

The irradiation of the reorganized samples, either initial or annealed films, with unpolarized light at 365 nm establishes a large disturbance in the lamellar system by forming a high cis to trans ratio of the azobenzene isomers. The optical in-plane anisotropy decreases and the film becomes optically isotropic

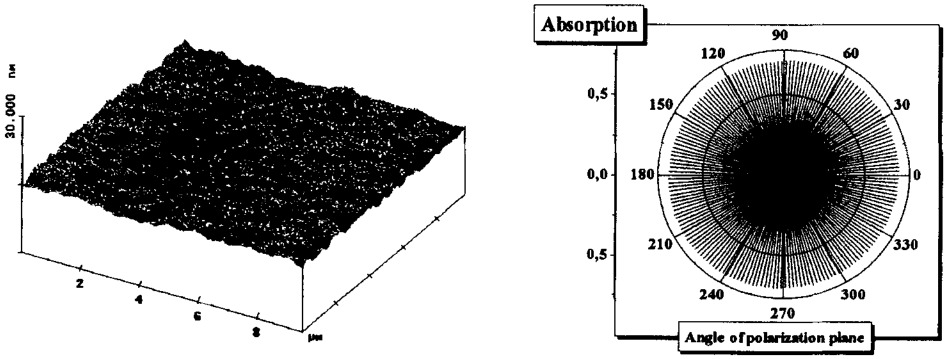

FIGURE 8 AFM image and angular dependent absorbance at 335 nm after unpolarized irradiation of a 64 layer assembly of 1 at 365 nm (3.2 mJ/cm^2).

The crooked geometrical shape of the cis isomers supports the destruction of the lamellar order and the optical in-plane anisotropy of the films decreases to zero. After an intermediate increase of surface roughness a general flattening of the interface was observed (Figure 8). The average peak height and mean roughness decrease dramatically to give values of 0.254 and 0.161 nm.

Unpolarized VIS irradiation

Upon irradiation with unpolarized light at 436 nm (1.8 mJ/cm^2) a steady state with a high amount of trans azobenzene moieties was established. A new lamellar order is photochemically reinduced while the double layer spacing of 52Å is the same as that of the annealed film. The aggregation behaviour at the polymer air interface is reproducibly changed and is particularly typical. The formation of large irregular aggregates at the surface was always detected. The clusters include total height differences up to 10 nm indicating, that the platelets range over a distance of up to four monolayers and they contain several hundreds of side groups each (Figure 9). Average values for height and roughness were 8.835 nm and 3.54 nm respectively. Obviously, there is a different depth dependence of the reorientation process in neighbouring domains found by X-ray grazing incident diffraction (GID).

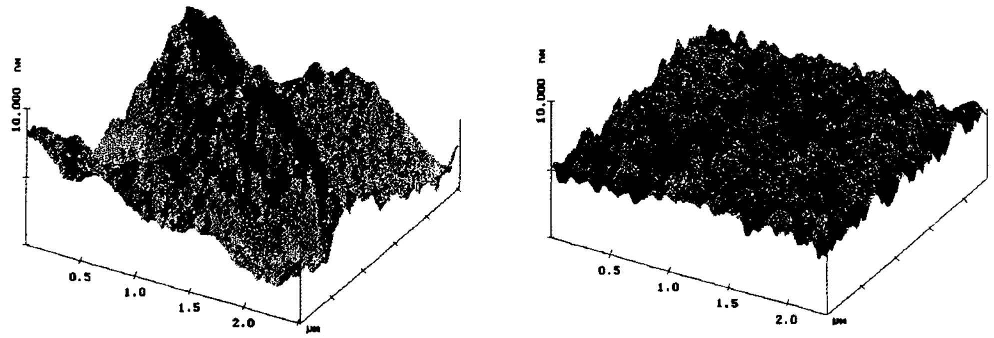

FIGURE 9 AFM images of the polymer air interface after unpolarized illumination at 436 nm with 1.8 mJ/cm^2 (left) and after polarized irradiation at 436 nm (right).

Polarized VIS irradiation

While the irradiation with unpolarized light led to a loss of the initial or photoinduced optical anisotropy the exposure with linearly polarized light at 436 nm induced a new optical in-plane anisotropy perpendicular to the electric field vector of incident light.

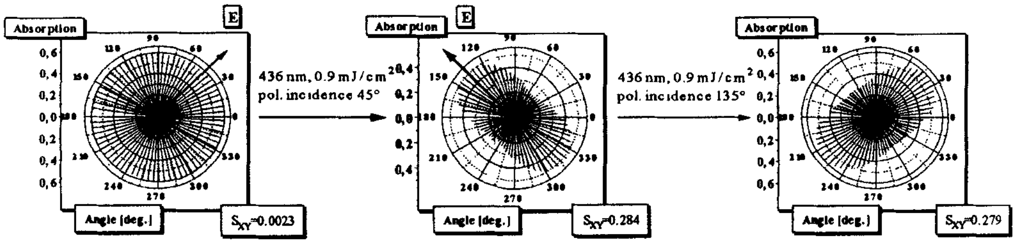

FIGURE 10 Optical anisotropy had been reinduced after polarized illumination at 436 nm. The change of orientational partition had been carried out by variation of the polarization plane of actinic light.

The direction of optical anisotropy could be modified between different orientational partitions by means of corresponding changes in the polarization plane of the incident polarized beam (Figure 10).

Changing the trans to cis ratio of the isomers back and forth by means of polarized incidence at 365 and 436 nm ,respectively, produces characteristic features for both states which are different from the platelets or the total flatness of the interface when irradiated with unpolarized light. Repeated cycles of irradiation yield a flat surface which allows increasing resolution of the platelets (Figure 11). This offered the chance to screen a high resolution AFM micrograph to visualize the interface at a molecular level.

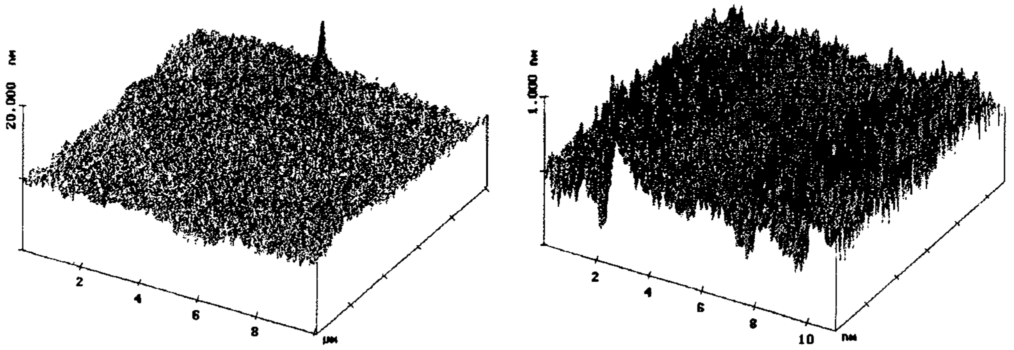

FIGURE 11 AFM image of a thermally relaxed sample of a 86 layers LB film after repeated polarized cycles (63°C) at 365 and 436 nm respectively (left). A high resolution image of the surface at molecular resolution in the nm scale is shown (right).

Figure 11 (right) shows a molecularly resolved image of the interface of a 86 layer per side transformed LB film of polymer 1. This AFM micrograph displays a 10.9x10.9 nm area irradiated with polarized light at 436 nm (polarization plane 45°, scan direction 230°). It shows 624 regular peaks having an average distance of 3.9Å. Measured values from GID investigations for the side chain distances range from 3.8 to 4.2Å. Surprisingly, only small parts of the side groups have close contact with the interface due to the average peak height of 0.158 nm (threshold 0.107 nm, mean roughness from 0.053 to 0.065 nm, covariance 0.171 nm^2)

Conclusions

The supramolecular structure of Langmuir-Blodgett multilayers built up by an amphotropic side group polymer with photochromic azobenzene moieties was modified upon annealing and irradiation. Thus, the photoisomerization of azobenzene side groups generates a change in the vertically layered structure, the optical in-plane anisotropy and the surface structure on irradiation with light of different wavelengths and polarization.

The initially tilted LB structure characterized by the 46Å double layer spacing and an optical anisotropy next to the dipping direction was irreversibly destroyed on annealing or irradiation in the UV region. However, a new layered structure was rebuilt upon annealing or irradiating the samples with VIS light respectively. The new lamellar structure was identified by the characteristic 52Å double layer distance and the absence of optical in-plane anisotropy. The structure identified is very similar to the smectic bilayer assemblies found in the bulk phase of the investigated polymer. The bilayer structure was reversibly destroyed upon irradiation with light at 365 nm wavelength but rebuilt on exposure with light at 436 nm.

The selforganization of the rod-like trans azobenzene moieties influences also the surface structure. Thus, a multilayer assembly containing a high amount of cis isomers appears flat at the polymer air interface with no significant subdomains observed whereas films with a high amount of mesogenic trans isomers show more or less regular features at the surface.

The AFM and SAXS investigations show a polydomain structure of the initial LB layer systems as well as of the transformed films. These domains are characterized by an almost uniform alignment of the azobenzene side groups and a definite tilt angle of the azobenzene moieties to the surface normal. The probability of excitation by the incident beam decreases with rising angle between electric field vector of light and transition moment of the aligned trans azobenzene side groups.

On continued irradiation within the steady state at 457 nm a modification of the orientational partition of the azobenzene units was achieved by an angular dependent photoselection process when irradiated with linearly polarized light. The disturbance at this wavelength is small, however a number of isomerization steps causes a directed reorientation of the tilted azobenzene groups to a preferred orientation perpendicular to the plane of incident light. In a certain number of domains where the tilt angle of the side groups forces the probability of excitation with respect to the incident polarized light beam the photoreaction took place.

The disturbance is due to the transformation of molecular shape of the photochromic moieties in the domains. Neighbouring domains with an inclined alignment of side groups were less affected by these changes in shape. This process results in a different macroscopic change of the neighbouring domains with an extent up to four times the monolayer spacing in height which was monitored by AFM and X-ray reflectometry. The transformation processes at the interface have a major influence on the lamellar structure next to the surface.

Unpolarized irradiation excites all azobenzene side groups only in dependence of the tilt angle between transition moment and the surface normal in a certain time and forces a photoreaction of the photochromic moieties. So, the extent of cluster formation and fading is much more higher than in case of polarized incidence. This is not only due to the higher intensity of the incident light upon unpolarized exposure but to the missing selectivity of excitation and the following transformations of the surface characteristics.

The supramolecular structure of LB multilayer assemblies built up by an amphotropic copolymer was reversibly modified by the light-induced change of mesogenity and the related tendency to selforganization of azobenzene moieties within the films. Optical in-plane anisotropy was reversibly induced and modified by a directed reorientation process caused by angular-dependent photoselection. The related photochemically induced variation of the surface properties by different steady states and the photoselection process results in a better understanding of the „command surface“ effect[22-26]. A more detailed explanation of the behaviour of different aggregates and the above mentioned effect will be discussed in a forthcoming paper.

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