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Optically Induced Birefringence and Surface Relief Gratings in Composite Langmuir−Blodgett (LB) Films of Poly[4′-[[2-(methacryloyloxy)ethyl]ethylamino]-2-chloro-4-nitroazobenzene] (HPDR13) and Cadmium Stearate

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ABSTRACT: Photoinduced trans−cis−trans isomerization, optical storage, and surface relief gratings are demonstrated in mixed Langmuir−Blodgett (LB) films of poly[4′-[[2-(methacryloyloxy)ethyl]ethylamino]-2-chloro-4-nitroazobenzene] (HPDR13) and cadmium stearate (CdSt). The trans−cis−trans photoisomerization of the azobenzene chromophores from HPDR13 in the mixed LB film was achieved with a circularly polarized laser light. The birefringence induced by a linearly polarized laser light decreased with the number of layers and increased with the weight percentage of HPDR13 in the mixed LB film. The surface relief gratings recorded by exposing the mixed LB film to an interference pattern produced by the laser light were visualized through atomic force microscopy (AFM). Interestingly, it seems that the nonphotoactive CdSt domains have also migrated along with HPDR13 while recording the surface relief gratings.

Introduction

Azobenzene functionalized polymers are candidate materials for constructing various molecules based optical devices, exploiting features from nonlinear optics,[1−3] optical switching,[4,5] optical storage,[6−10] surface relief gratings,[11−14] holograms,[15−16] optical modulators,[17] and command surfaces for aligning liquid crystals.[18−20] One of the main properties to be exploited is the photoinduced reversible trans−cis−trans isomerization of the azobenzene group, which is usually completely feasible and reversible in the solution phase,[21] but not so straightforward in the solid state owing to the need of a "free volume" around the azo group.[22] The trans−cis−trans isomerization induced by a circularly polarized laser may be applied in optical switching, while the photoisomerization accompanied by molecular reorientation induced by a linearly polarized light can be useful for optical storage applications. Surface relief gratings can be produced by isomerization of the azobenzene chromophore, which is accompanied by large-scale migration of the molecule, induced by an interference pattern.

For polymers with covalently attached azobenzene chromophores, in particular, the trans−cis conversion and its reversibility have been studied as a function of several factors: type of substituent attached to the azobenzene ring,[23] nature of the parent polymer,[7] and the presence of spacer groups[24] and of interactive neighboring groups.[25] Among them, the proper choice of substituents is of prime importance for fine-tuning the optical characteristics of the azobenzene chromophore. For instance, stable cis and trans isomers can be obtained with azobenzenes with no active substituents, which is useful for optical switching.[26] Azobenzenes attached to push−pull substituents, on the other hand, exhibit fast trans−cis photoisomerization and cis−trans thermal conversion, which can be conveniently used in optical storage applications and in the creation of surface relief gratings.[26]

In addition to the search for novel materials displaying the required optical properties for a specific application, one important issue is related to the degree of control in molecular structures, which is not offered by the conventional casting and/or spin coating fabrication methods of polymeric films. For instance, Natansohn et al.[27] have emphasized the influence of film thickness on the optical storage properties of cast polymeric films containing azobenzene. In sufficiently thick samples, the intensity of the writing beam may vary substantially throughout the film, which affects the writing time needed to reach maximum birefringence, resulting in an uneven writing. Such problems may be alleviated if a technique such as the Langmuir−Blodgett (LB) method[28] is employed, since great control of film thickness and surface uniformity are provided. The LB technique has been used for producing amphiphilic azobenzene-containing films for optical switching[4,29] and mixed LB films of disperse red-19 isophorone polyurethane and cadmium stearate whose optical storage characteristics were investigated.[29] To our knowledge, no attempts have been reported aimed at building surface relief gratings out of LB films from azobenzene-containing polymers.

In the present work, we report on the photoisomerization, optical storage, and optically induced surface relief gratings of thin films of homopolymer of methacrylate derivative of disperse red-13, poly[4′-[[2-(methacryloyloxy)ethyl]ethylamino]-2-chloro-4-nitroazobenzene] (HPDR13) produced via the LB technique. For obtaining good quality LB films, we employed the mixed LB film approach in which HPDR13 was co-deposited with cadmium stearate, as this methodology has proven to produce uniform and reproducible ultrathin films of polymeric materials.[30−32] The monolayer characteristics

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and the LB film properties for HPDR13 and the mixtures of HPDR13 and cadmium stearate have already been reported in refs 33 and 34.

Experimental Section

The homopolymer of methacrylate derivative of disperse red-13 (HPDR13) was synthesized according to the procedure reported elsewhere.[33] The fabrication procedures for composite LB films of HPDR13 and cadmium stearate were reported in ref 34. Basically, a chloroform solution containing different mole percentages of HPDR13 and stearic acid was spread on an aqueous subphase that contained cadmium chloride (4×10^{-4} M) and sodium bicarbonate (5×10^{-5} M), to keep the pH at 6.0. Ultrapure water for the subphase was supplied by a Milli-RO coupled to a Milli-Q purification system from Millipore (resistivity 18.2 MΩcm). Monolayer studies and multilayer LB film deposition were carried out with a KSV 5000 LB system placed on an antivibration table in a class 10 000 clean room at room temperature. BK7 glass and calcium fluoride plates were used as substrates which were cleaned thoroughly prior to use. Mixed monolayers were transferred at a dipping speed of 3 mm/min.

The photoisomerization characteristics of HPDR13 were studied in chloroform solution as well as in LB films with either of two light sources: unpolarized light from a 1000 W Oriel 6100 series mercury−xenon (Hg−Xe) lamp equipped with commercially available filters for required wavelengths or a circularly polarized unfocused laser light from an argon ion laser operating at 514 nm. The unpolarized and circularly polarized lights were used to avoid reorientation of the azo groups and the beam was unfocused in order to avoid heating the sample at the point of incidence. When the Hg−Xe lamp was used to induce photoisomerization, the changes in the absorption spectral characteristics of the azobenzene chromophore were monitored by recording the UV−vis spectra before and after irradiation. However, when the laser light was employed, the photoisomerization was measured “in situ” with a low intensity probe beam. The pump beam, which induces the photoisomerization, was modulated by means of a mechanical chopper. The probe beam, passing through the sample and coinciding with the pump beam, was analyzed with the use of a digital oscilloscope. The change in transmittance of the probe beam through the film could therefore be monitored. For the sake of comparison, photoisomerization studies were also performed with the DR13 dye and methacrylate DR13 monomers in chloroform solutions. The optical storage experiments were performed as follows: The optical birefringence was induced in the LB film using a diode-pumped, frequency doubled, linearly polarized Nd:YAG continuous laser at 532 nm with a polarization angle of 45° with respect to the polarization orientation of the probe beam (reading beam). The power of the writing beam was 2.9 mW for a 2 mm spot in most experiments, except in the case where the power of the laser light was varied systematically for studying its influence. A low power He−Ne laser light at 632.8 nm passing through crossed polarizers was used as the reading beam to measure the induced birefringence in the sample. Surface relief gratings on the mixed LB films were recorded under ambient conditions with the interference pattern produced by a linearly p-polarized Nd:YAG continuous laser at 532 nm. To produce the interference pattern, the laser beam is splitted into two components. The first one impinges directly on the sample, and the second is reflected onto the sample by a mirror. The angle between the two beams is approximately 12°. The surface morphology of the LB film was investigated by atomic force microscopy (AFM) using a Nanoscope IIIa system from Digital Instruments before and after the gratings were recorded. The topographical and phase images were obtained in the contact and tapping modes, respectively. In the contact mode, a triangular shaped 200 μm long silicon nitride cantilever with a spring constant of 0,06 N/m was employed. The applied force was 6 nN with a scan rate of 2 Hz. In the tapping mode, a 250 μm long silicon cantilever was used with a scan rate of 2 Hz.

Results and Discussion

The homopolymer HPDR13 is able to form a reasonably stable and transferable monolayer, but attempts to produce thick LB films were unsuccessful.[33] However, mixed monolayers of HPDR13 and cadmium stearate could be transferred uniformly up to one hundred layers or so.[34] Such LB films with different contents of HPDR13 and cadmium stearate and different numbers of layers were characterized by UV−vis, FTIR, and XRD techniques, as reported in ref 34. For a given composition, the absorption at 500 nm, which is characteristic of the $\pi-\pi^*$ transition of the azobenzene chromophore, increased linearly with the number of layers, indicating the transfer of an equal amount of HPDR13 in each deposition. The UV−vis and FTIR spectroscopies revealed the transfer of both HPDR13 and cadmium stearate, while the X-ray diffraction results indicated that they are present in separate domains.[34] In this paper we concentrate on photoisomerization, optical storage and surface relief gratings of mixed LB film of HPDR13 and cadmium stearate.

Photoisomerization Experiments. When light with appropriate wavelength and intensity impinges on an azobenzene-containing material, it induces geometrical isomerization of the azobenzene group. This results in the transformation of one photostationary state that contains a larger number of the thermodynamically more stable trans isomer to another photostationary state with a higher population of the cis isomer. When the light is switched-off, the cis isomer reverts back thermally to the trans isomer, the rate of which depends on the azobenzene substituents. This trans−cis−trans photoisomerization can be conveniently followed in several ways: (i) by reading the change in absorbance/transmittance at a particular wavelength, since trans and cis isomers have different absorption patterns,[21] (ii) by detecting the change in the area per chromophore, as the trans form occupies a smaller volume,[35] and (iii) by measuring the change in dipole moment from surface potential measurements, since the trans form possesses smaller dipole moment than the cis isomer.[4,7] This trans (off state) to cis (on state) conversion is reversible and can be repeated a number of times without any considerable hysteresis or material degradation.

We have studied the photoisomerization of azobenzene chromophores by using either a mercury−xenon lamp or a circularly polarized unfocused laser light. In a first set of experiments, chloroform solutions of DR13, methacrylate monomer of DR13 and HPDR13 were irradiated with the Hg−Xe lamp. The spectrum of HPDR13 (mainly trans isomer) showed two absorptions characteristic of the azobenzene chromophore at 280 nm and at 500 nm. No change in the UV−vis spectrum was observed even after prolonged irradiation; thus, the spectrum of the cis isomer could not be observed. The spectra of mixed LB films of HPDR13 and cadmium stearate were not affected either. The lack of change is explained as follows. The azobenzene compounds employed here possess push−pull (electron withdrawing nitro group and electron donating amino group) substituents, for which the cis isomer formed upon irradiation is expected to be highly unstable and revert back immediately to the initial and more stable trans state by thermal means.[7] The time interval between irradiation and the UV−vis spectral measurements was obviously long, and therefore when the spectra were taken, all azobenzene chromophores had returned to their initial trans state.

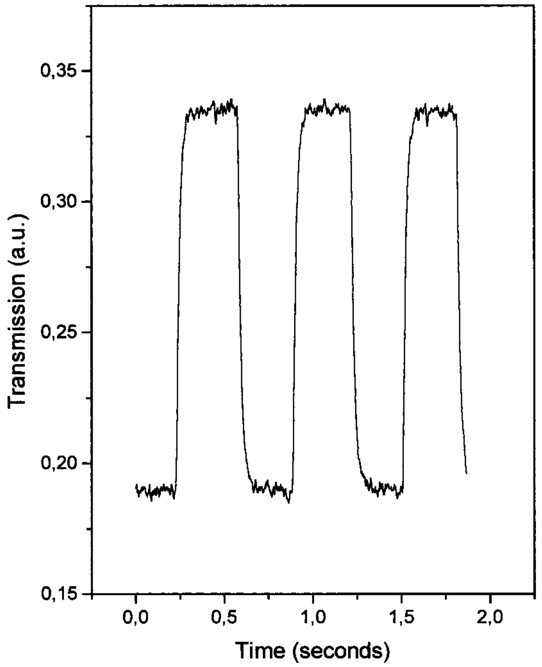

Figure 1. Temporal evolution of the optical transmittance as the circularly polarized laser light is switched on and off, illustrating the trans–cis–trans photoisomerization cycles of HPDR13 in chloroform (10^{-4} M).

However, when in situ measurements were carried out using a circularly polarized laser light, as described in the Experimental Section, a clear trans–cis–trans photoisomerization could be observed for all three compounds in chloroform and in the mixed LB films of HPDR13 and cadmium stearate. Typical photoisomerization characteristics of HPDR13 polymer in chloroform solution are shown in Figure 1. When the circularly polarized laser light (80 mW) is on, the transmission increases since the cis isomer has a lower absorptivity at the wavelength of the probe beam (514 nm) than the trans isomer. However, as the light is switched off, the transmission decreases to the original level, which is indicative of the cis–trans conversion. The percentage changes of transmission of the probe beam for DR13, methacrylate monomer of DR13 and HPDR13 are about 20, 150 and 90, respectively. The time for cis–trans or trans–cis conversions was obtained by fitting the experimental curves with a first-order exponential function. While the trans to cis conversion time is approximately 30 ms in both the methacrylate monomer of DR13 and HPDR13, the cis to trans conversion time is considerably shorter for HPDR13 (18 ms) than for the DR13 monomer (60 ms). These fast cis–trans thermal conversion times explain our failure in observing any absorption spectral changes in the photoisomerization experiments in which there was a time lag for measuring the spectra. Similar photoisomerization characteristics were observed with mixed LB films of HPDR13 and cadmium stearate (75:25 w/w 41 layers) with the use of circularly polarized light (60 mW), as shown in Figure 2, where the only significant difference is in the slower cis–trans thermal relaxation in the LB films.

Optical Storage Experiments. If a linearly polarized, instead of a circularly polarized, laser light is used, orientation of the azobenzene chromophore can be induced after a series of trans–cis–trans isomerization processes with accompanying molecular reorientations.[7] Upon absorbing a linearly polarized light, the molecule undergoes a series of trans–cis–trans conversions and after each such conversion may adopt any orientation including its original one. The only exception are those molecules whose dipole moment was originally perpendicular to the polarization direction of the light and therefore do not absorb light to undergo the conversions. At the end of several cycles, there will be a net population of molecules oriented in the direction perpendicular to the light polarization, thereby resulting in birefringence in the film structure (WRITE). When the light source is switched off, some molecular relaxation occurs, but a considerable number of molecules remain oriented, thus giving rise to a stable birefringence pattern (STORE). The creation of birefringence can be inferred by the change of transmittance of the weak probe beam that passes through crossed polarizers (READ). This birefringence pattern can be completely erased by heating or overwriting the test spot with circularly polarized light (ERASE).

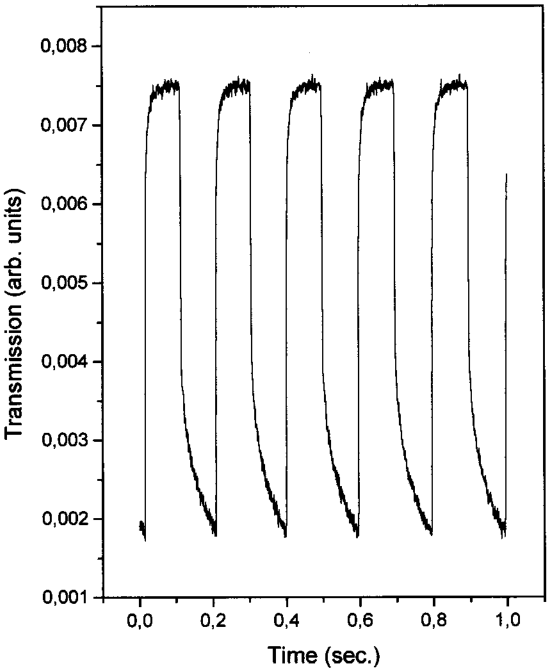

Figure 2. Same as Figure 1, but for a 100-layer mixed LB film of HPDR13 and cadmium stearate (50:50 w/w)

The results of typical optical storage experiments performed with a composite LB film of HPDR13 and cadmium stearate (100 layers) are presented in Figure 3. For the sake of clarity, the overall change in transmission, related to the birefringence, is normalized between 0 and 1. Before the writing beam is switched on, no transmission of the probe beam that passes through the film and crossed polarizers was observed. This indicates that the chromophores were oriented randomly. However, when the writing beam was switched on at point A, the transmission increased, reaching 80% of the saturation value in 3.8 s and remaining at the saturation value as long as the light source is on. Such an increase in transmission is related to the induced birefringence owing to the orientation of chromophores. When the writing beam was switched off at point B, the transmission decreased sharply, reducing to nearly 70% and 35% of the saturation value after a time span of 1.6 and 140 s, respectively. If the sample was left to relax, the transmission at point C (about 35% of saturation value) remained practically the same for several days. Hence, a significant number of molecules

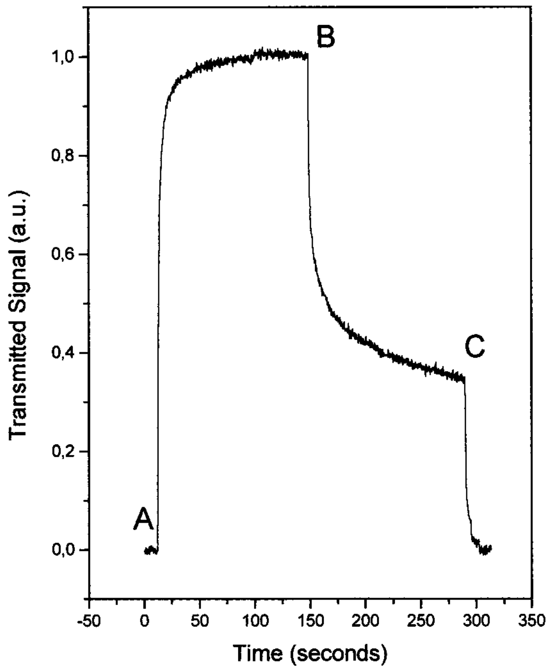

Figure 3. Writing and erasing sequence on a 100-layer mixed LB film of HPDR13 and cadmium stearate (50:50 w/w)

remain oriented, with the birefringence being maintained even after the writing beam was switched off. This induced birefringence could nevertheless be erased either optically—by overwriting the test spot with circularly polarized light—or thermal means—by heating the sample to a higher temperature which randomizes the chromophores orientation. Several cycles of writing and erasing could be performed without any significant change in the maximum induced birefringence and material degradation.

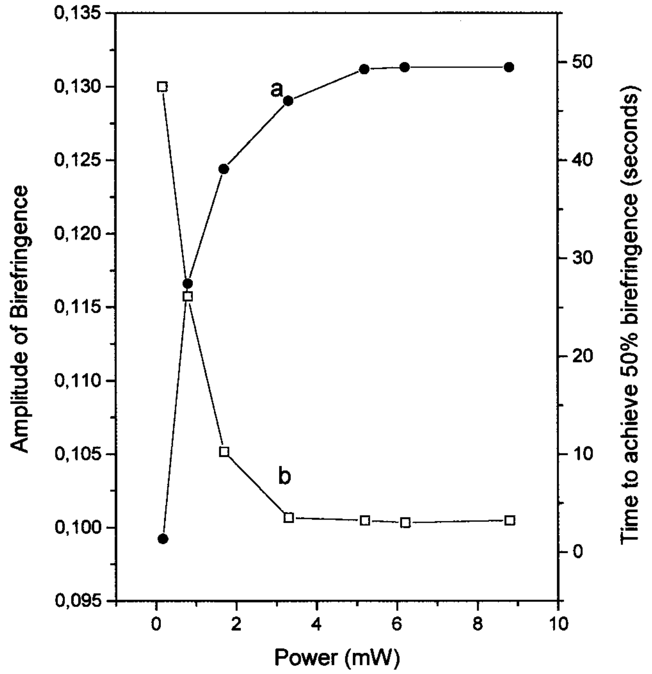

Figure 4. Dependence on the laser power for the amplitude of induced birefringence (curve a) and time to achieve 50% of the maximum birefringence (curve b), in a 100-layer mixed LB film of HPDR13 and cadmium stearate (50:50 w/w). The lines are drawn to guide the eye.

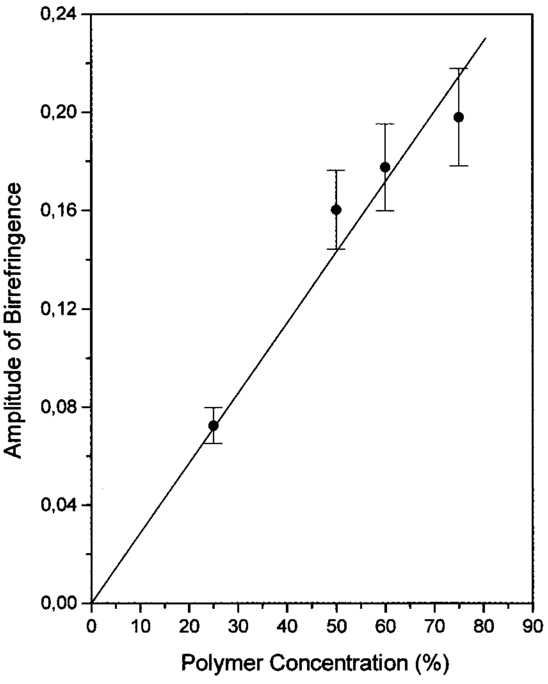

Figure 5. Amplitude of the induced birefringence vs weight percentage of HPDR13 in a 41-layer mixed LB films of HPDR13 and cadmium stearate. The line is drawn to guide the eye.

A study was made of the influence on the induced birefringence of the laser power, composition and number of layers of the mixed LB films. Figure 4 shows the change in maximum birefringence and the time to achieve 50% of maximum birefringence as a function of the laser power for a 100-layer composite LB film of HPDR13 and cadmium stearate. The induced birefringence increases with the laser power up to 2 mW or so, after which saturation is reached (curve a). This means that a laser power of about 2 mW is sufficient to induce the maximum birefringence in a 100-layer thick mixed LB film of HPDR13 and cadmium stearate, which is comparable to the value observed for a 61-layer mixed LB film of disperse red-19 isophorone polyurethane and cadmium stearate.[31] The time to achieve 50% of maximum birefringence decreased drastically with the increase in power of the writing beam, again up to 2 mW (curve b). For a given number of layers (say 41 layers) the amplitude of the induced birefringence increased near linearly with the weight percentage of the HPDR13 in the mixed LB films, as shown in Figure 5. This can simply be attributed to the increase in the number of chromophores as the HPDR13 contents are raised. The absolute value of birrefringence of a 41 layers, 75% weight HPDR13 film is 0.19, which is higher than that observed for similar polymers, such as pDR13A (poly-[4′-[[2-(acryloyloxy)ethyl]ethylamino]-2-chloro-4-nitroazobenzene).[26] This can be attributed to the ordered packing of the LB films which contributes to the optically induced birrefringence. The time to achieve 50% of maximum birefringence and the remaining birefringence when the writing beam was switched off were not affected by change in composition. These results point to a photoisomerization of molecular origin.

Optical storage experiments were also performed with mixed LB films of HPDR13 and cadmium stearate with different numbers of layers, but with the same composition (50:50 w/w). The maximum birefringence decreases with the number of layers up to 100 layers or so, as shown in Figure 6. This behavior can be related to the

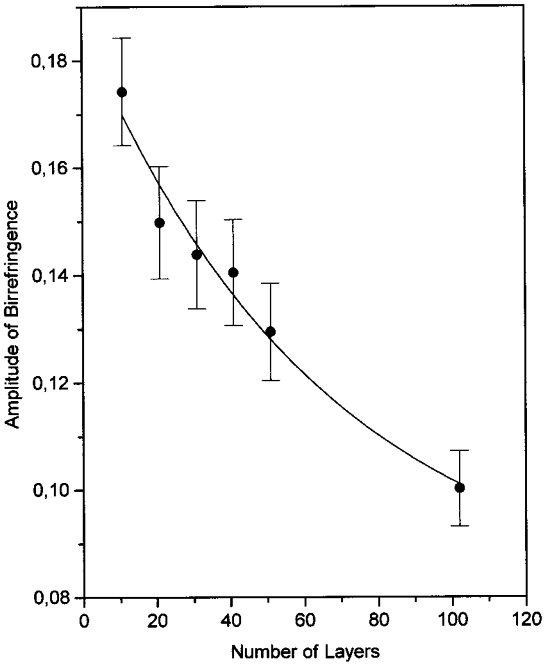

Figure 6. Amplitude of the induced birefringence as a function of the number of layers for mixed LB films of HPDR13 and cadmium stearate (50:50 w/w). The line is drawn to guide the eye.

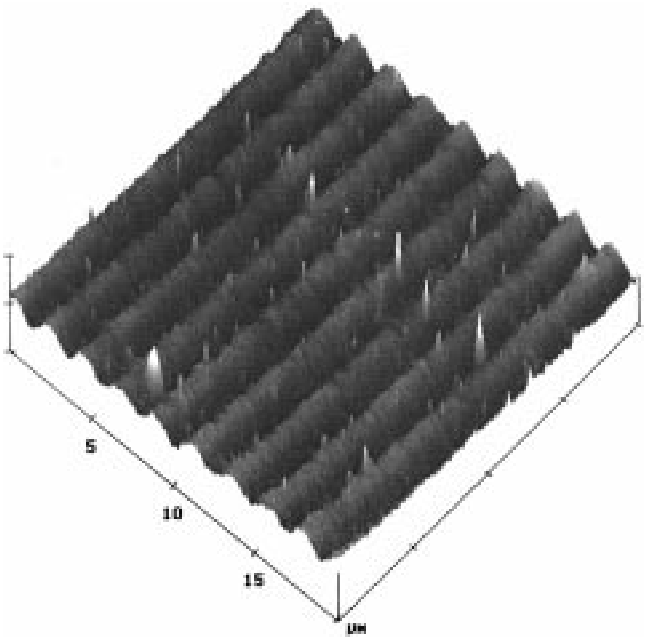

Figure 7. Atomic force microscopy 3-D topography image (20 μm × 20 μm × 200 nm) of the surface relief gratings on a 100-layer mixed LB film of HPDR13 and cadmium stearate transferred onto glass.

decrease in ordering in the LB film when a large number of layers are transferred. To verify whether the birefringence will tend to the value of a bulk film for thicker LB films, further experiments are necessary. The time for achieving 50% of maximum induced birefringence and the remaining birefringence after switching off the writing beam were not affected significantly upon increasing the number of layers. In summary, by changing composition and film thickness one may control the concentration of azobenzene chromophores and hence fine-tune the amplitude of maximum induced birefringence.

Optically Induced Surface Relief Gratings. When a film of azobenzene compounds is exposed to an interference pattern of laser beams, a large scale molecular migration is observed which leads to regularly spaced surface relief gratings on the film surface that can be visualized through atomic force microscopy (AFM). Such gratings seem to be formed via photoinduced trans–cis–trans isomerization of the azo chromophores in which the interaction of molecular dipoles with the electric field gradient of the laser light results in the wormlike physical movement of the molecule. The mechanisms involved in these processes have attracted great attention of late.[13,36–42]

The three-dimensional atomic force microscopy (AFM) picture of surface relief gratings created on a 100-layer thick mixed LB film of HPDR13 and cadmium stearate (50:50 w/w) deposited on a glass substrate is shown in Figure 7. The LB film was exposed to an interference pattern generated by a linearly p-polarized Nd:YAG continuous laser at 532 nm with a power of 180 mW/cm^2 for 3 min. It may be mentioned that no such regular gratings were seen on the film surface prior to the exposure to the interference pattern. The grating spacing was about 2.6 μm and the peak-valley height was in the range of 50–60 nm, which are comparable to the values reported in the literature.[11] The gratings were stable for months.

In the process of optimizing experimental conditions for creating stable physical gratings onto the surface of LB films, we made some interesting observations that are worth mentioning. When we used a low power laser (10 mW/cm^2) for creating the gratings, we did observe the diffraction of the He–Ne laser upon passing through the film, but no physical grating patterns could be seen in AFM pictures. The observed diffraction could be attributed to index gratings induced by the orientation of chromophores in a process similar to the optical storage. When a high power laser was used, gratings were formed over the laser area in which diffraction of white light could be seen with naked eyes. This film region was analyzed using UV–vis and FTIR spectroscopies. The transmission UV–vis spectra of both exposed and unexposed areas of a 100-layer mixed LB film of HPDR13 and cadmium stearate are shown in Figure 8. The striking differences are a decrease accompanied by a red shift in the absorption maximum from 500 to 520 nm. The red shift is still not fully understood, but two causes for the decrease in absorption are readily apparent. It may be related either to the diffraction of the source light while passing through the film, thus decreasing the light intensity reaching the spectrophotometer detector or to material decomposition in the laser light illuminated area. A prolonged exposure of a laser beam caused decomposition of the azobenzene polymer, poly(1-acryloyl-4-{4-(4-nitrophenylazo)phenyl]piperazine (p-ANPP),[43] but no such photoinduced decomposition was observed with the type of polymer employed in the present study.[43] The photoinduced decomposition of p-ANPP has resulted in drastic changes in UV–vis and FTIR spectra owing to the destruction of the azobenzene group and the presence of an amide group and the cyclic piperazine unit.[43] The absorption spectral changes of Figure 8 cannot simply be attributed to the destruction of the azobenzene group in the film material, since there is still a strong absorption in the region of 500–600 nm. Furthermore, as shown in Figure 9, no significant changes could be

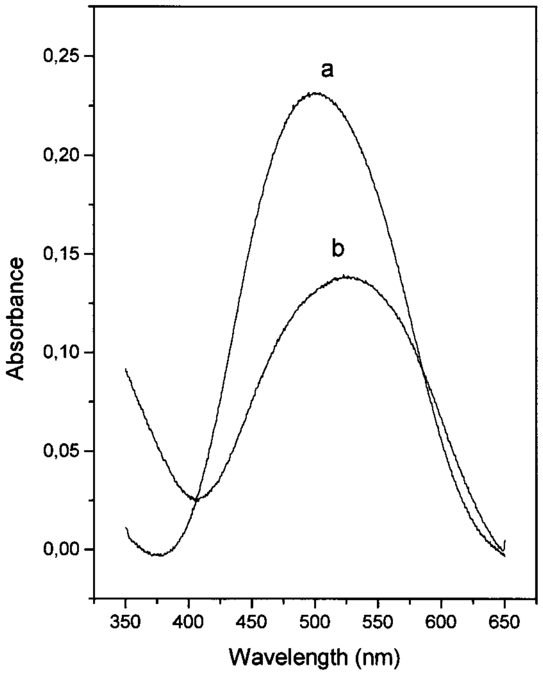

Figure 8. UV−vis spectra of a 100-layer mixed LB film of HPDR13 and cadmium stearate (50:50 w/w) on a glass substrate: (a) as deposited; (b) after prolonged exposure to the laser light.

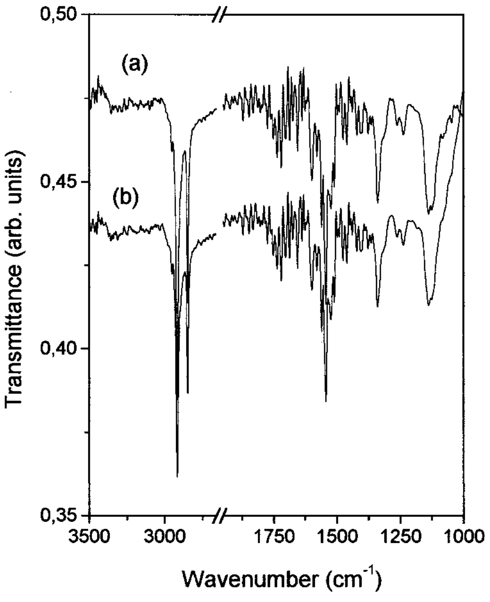

Figure 9. FTIR spectra of a 100-layer mixed LB film of HPDR13 and cadmium stearate (50:50 w/w) deposited on a calcium fluoride substrate: (a) as deposited; (b) after prolonged exposure to the laser light.

observed in the FTIR spectra obtained for both exposed and unexposed areas of the mixed LB film, which means that there is no significant compositional change of the film material upon exposure to the laser light. The vibrational absorption features for the unexposed area of the composite LB film is the superimposition of the characteristic FTIR patterns observed with pure HPDR13 and pure cadmium stearate as reported in ref 34. When this exposed area was analyzed through optical microscopy (500 magnification), it looked dark with a faint grating pattern.

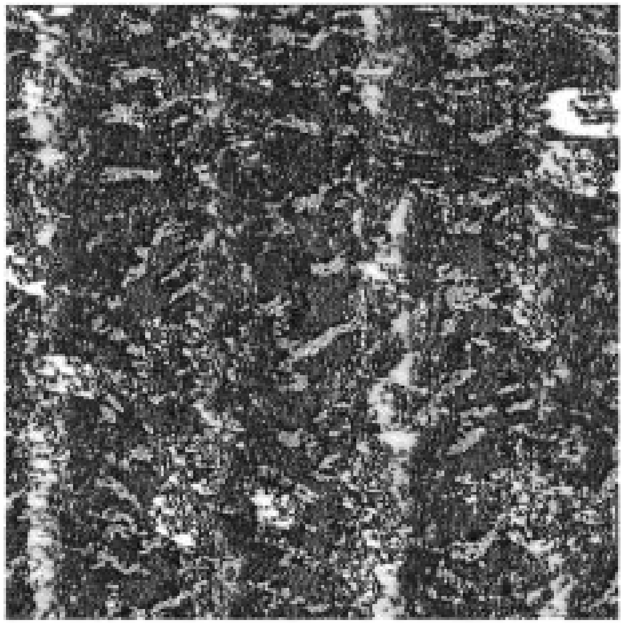

Figure 10. Atomic force microscopy phase image (10 μm × 10 μm) for the surface relief gratings on a 100-layer mixed LB film of HPDR13 and cadmium stearate deposited on glass.

The wormlike movement of azobenzene groups seems to be responsible for the migration of HPDR13 molecules while creating the gratings on the mixed LB film surface, but it is also interesting to investigate what happens to the cadmium stearate molecules. The HPDR13 and cadmium stearate are present as separate domains in the mixed LB film, as evidenced from XRD studies.[34] From the AFM image in Figure 7, it seems that the cadmium stearate domains have also moved along with HPDR13 molecules, which is corroborated by phase images of the surface in the tapping mode AFM, as shown in Figure 10. There are clearly two types of material with different viscoelasticity, which can be attributed to cadmium stearate and HPDR13 domains. However, it is difficult to identify exactly whether a domain is of cadmium stearate or HPDR13. Only the brighter domains that appear in Figure 10 could be measured and have dimensions varying from 50 to 1500 nm. The cadmium stearate domains have moved along with HPDR13 and hence they are present both in the peak and valley regions. A detailed study on the influence of linearly (both s- and p-polarized) and circularly polarized lights on the mechanism of grating formation and also using AFM for films with different cadmium stearate and HPDR13 compositions is under progress.

Conclusions

The possibility of using Langmuir−Blodgett films of poly[4′-[[2-(methacryloyloxy)ethyl]ethylamino]-2-chloro-4-nitroazobenzene] (HPDR13) for optical storage and for recording surface relief gratings has been demonstrated. The amplitude of the optically induced birefringence could be controlled by varying the number of layers (thickness) and the relative contents of HPDR13 in the mixed LB film. Regularly spaced surface relief gratings could be recorded on the surface of mixed LB films, which was visualized via AFM. Overall, the results obtained with multilayer LB films were similar to those of cast films of azobenzene polymers, which is especially promising owing to the added advantage of film thickness control and uniformity over larger areas offered by the LB technique.

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