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The influence of electrostatic and H-bonding interactions on the optical storage of layer-by-layer films of an azopolymer

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Abstract

The optical storage properties of layer-by-layer (LBL) films of a copolymer of methacrylic acid and 4-[[2-(methacryloyloxy)-ethyl]ethylamino]-2′-chloro-4′-nitroazobenzene (MA-*co*-DR13) alternated with the cationic poly(allylamine hydrochloride) are reported. The writing process is considerably slower than in cast films due to electrostatic and H-bonding interactions that hinder molecular orientation. The speed of the writing process can be increased if the LBL film is immersed into pure water prior to the storage experiments, probably because entrapped water helps preventing intermolecular interactions. This is a reversible effect and cannot be attributed to mere water absorption of the polymer film, since cast films of the same components do not exhibit the 'water effect'. It is also demonstrated that the films display sensing capabilities, with their optical storage properties being significantly affected by gushes of hot and humid air. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Layer-by-layer; Optical storage; Azobenzene

1. Introduction

The photoisomerization of azochromophores in azobenzene-containing polymers has been investigated for a variety of applications and fundamental studies [1–4]. In particular, optical storage can be achieved because after several cycles of *trans–cis–trans* isomerization induced by a linearly polarized laser, birefringence and dichroism may be generated as a result of a net population of chromophores oriented perpendicularly to the laser polarization direction [5]. Photoisomerization is also the main process explored in the one-step formation of surface-relief gratings, all-optical processing [6], which involves large-scale mass transport of the macromolecules. In most studies, spin-coated or cast films are employed, but reports have also been made with polymer samples obtained with the Langmuir–Blodgett (LB) technique, especially for optical storage [7] and even for the formation of surface-relief gratings [8]. The first attempts to investigate the photoisomerization properties of azobenzene-containing polymer films fabricated with the now popular electrostatic layer-by-layer (LBL) technique (also referred to as self-assembly of polyanionic and polycationic structures) are very recent [9]. In this paper, we report on the optical storage properties of LBL films of a copolymer of methacrylic acid and 4-[[2-(methacryloyloxy)-ethyl]ethylamino]-2′-chloro-4′-nitroazobenzene (MA-*co*-DR13) alternated with the polycationic poly(allylamine hydrochloride) (PAH). Particular emphasis is given to the importance of the electrostatic and H-bonding interactions prevailing in this type of film, which makes the photoisomerization somewhat difficult to occur. As a result, writing information via several photoisomerization cycles takes much longer than in the spin-coated or cast films. The accelerating effect achieved by immersing the polymer samples into water prior to the isomerization measurements is attributed to entrapped water that appears to interact with the polymers macromolecules in such a way as to counterbalance the slowing effect of the electrostatic and H-bonding interactions.

2. Materials and methods

PAH and methacrylic acid were purchased from Aldrich

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Co. The synthesis of the monomer 4-[[2-(methacryloyloxy)-ethyl]ethylamino]-2′-chloro-4′-nitroazobenzene was performed by the esterification reaction of methacryloyl chloride and the commercial dye Disperse Red 13 (DR13) supplied by Aldrich [8]. The copolymerization of the monomer and methacrylic acid was performed by radical solution polymerization, using a mixture of *N*,*N*-dimethylformamide (DMF) and methyl-ethyl ketone (MEK) (3:1, v/v) as solvent and AIBN as initiator, at 80 °C for 9 h. The absence of non-reacted monomers in the final copolymer was confirmed by thin layer chromatography. The chemical structures of PAH and MA-*co*-DR13 are shown in Fig. 1. The UV–vis spectra of copolymer cast films on a quartz plate were recorded using a Hitachi U-2001 spectrophotometer and resulted in a broad band centered around 480 nm. The FTIR spectra, recorded as cast films from MEK on a silicon window in a Nicolet 560 instrument, displayed the following main absorption bands (in cm^{-1}) characteristics of both comonomers: 3300–3200 cm^{-1} (broad, OH characteristic of carboxylic acid), 2917 and 2850 cm^{-1} (CH_2 stretching), 1732 cm^{-1} (C=O ester stretching), 1700 cm^{-1} (C=O, carboxylic acid), 1599 and 1500 cm^{-1} (C=C, ring stretching), 1518 and 1336 cm^{-1} (NO_2), 1242 cm^{-1} (C(=O)–O), 1252 and 1134 cm^{-1} (O–C–C, ester group). The copolymer molecular weights were determined by HPSEC using THF as eluent and polystyrene standards ($M_w = 101\,700$ and $M_w/M_n = 3.7$). The azo comonomer content in this copolymer, determined by UV–vis spectroscopy using DR13 as standard, was 71 wt% (or 34 mol%). Aqueous solutions of PAH and MA-*co*-DR13 were prepared in concentrations of 0.15 and 0.5 g/l, respectively, and the pH of the solutions was adjusted at 10.0 with NH_4OH. Glass slides were rendered highly hydrophilic using the RCA Method [10] and used as substrates. Multilayers were assembled by the alternated immersion of the substrate into the polycationic and polyanionic solutions for 3 min each at room temperature (20 °C). After each deposition, the substrates were rinsed for 1 min in an aqueous washing solution under stirring. The washing solution had the same pH of the deposition solutions. The films were then dried under a nitrogen flow. The buildup of the multilayers was monitored by UV–vis absorption spectroscopy. Thickness measurements were carried out using a Talystep-Taylor Hobson profilometer. Fluorescence measurements were carried out in a Renishaw Research Raman Microscope System RM 2000. A Leica microscope and a 50 × -microscope objective were used to focus the laser beam onto a spot of ca. 1.0 $\mu\mathrm{m}^2$. The fluorescence and Raman spectra were recorded at 20 °C using the 633 and 514.5 nm laser lines.

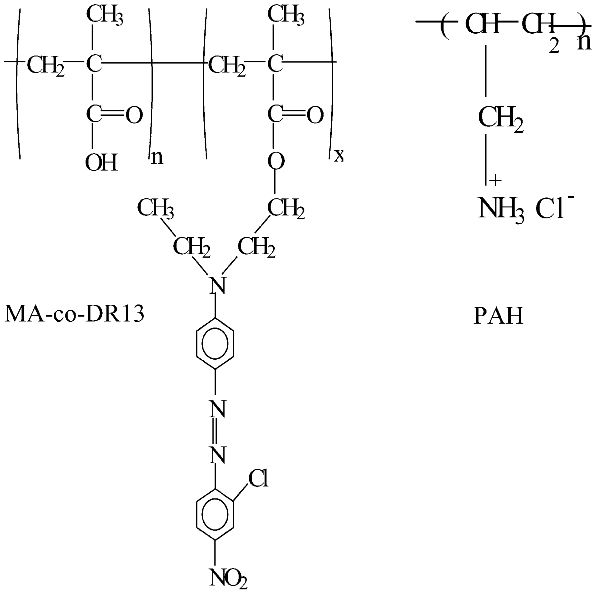

Fig. 1. Molecular structures of MA-*co*-DR13 and PAH used for the ELBL assembly.

The experimental setup used in the optical storage experiments is similar to that previously reported [8]. The optical birefringence was induced in the film using a linearly polarized Nd/YAG continuous laser operating at 532 nm (writing beam) with a polarization angle of 45° with respect to the polarization direction of the probe beam. The power of the writing beam used in the experiments was varied from 17 to 19 mW for a 2 mm spot size. The change in the transmission of a low power He–Ne laser (reading beam) operating at 632.8 nm, which passes through two crossed polarizers and the sample, was measured with a photodiode.

3. Results and discussion

3.1. Formation of multilayers of PAH/MA-co-DR13

A linear increase is observed in Fig. 2 for the maximum absorbance with the number of deposited bilayers for the PAH/MA-*co*-DR13 films, indicating that the same amount of material is adsorbed at each deposition step. Absorption

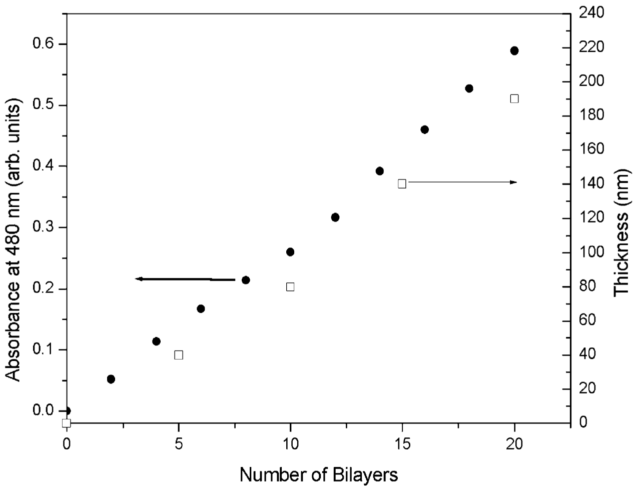

Fig. 2. Maximum absorbance and film thickness as a function of the number of deposited bilayers for a PAH/MA-*co*-DR13 film.

is entirely due to MA-*co*-DR13 since PAH does not absorb in this particular UV–vis spectral window. In Fig. 2 is also shown the thickness of the LBL films as a function of number of deposited bilayers, where the slope yields an average thickness of ca. 100 Å per bilayer. Such large thickness, in contrast to the molecularly thin layers obtained from strong polyelectrolytes, is due to the participation of H-bonding interactions in the adsorption process, in addition to the ionic forces [11,12].

3.2. The effect on optical storage from wetting the PAH/MA-co-DR13 film

The optical storage can be achieved in LBL films of PAH/MA-*co*-DR13 is shown in Fig. 3. The results correspond to the writing–erasing process for a 40-bilayer film that was subjected to a linearly polarized light at point A. After reaching the maximum signal, the laser was switched off at point B. Some relaxation followed, but a considerable amount of chromophores remained oriented as indicated by the residual signal (60% of the maximum value). The erasure was performed by impinging circularly polarized light onto the sample, at point C in the figure, which randomizes the chromophores orientation and eliminates the induced birefringence. At point B the birefringence was estimated as $\Delta n = 0.068$ according to Eq. (1)

$$\Delta n = \frac{\lambda}{\pi d}\sin^{-1}\sqrt{\frac{I}{I_0}} \tag{1}$$

where λ is the wavelength of the incident radiation, d is the film thickness, I_0 is the incident beam intensity and I is the intensity after the second polarizer.

It should be noted that the writing time for the LBL films is much longer than in spin-coated and LB films of similar azobenzene-containing polymers. For instance, writing times for the other types of film are in the order of 10–100 s, compared to over 1000 s time to attain the results shown in Fig. 3. There is evidence that the process becomes sluggish because of the electrostatic and H-bonding interactions in the LBL films that make it difficult for the molecular orientation induced by photoisomerization to proceed [9], and this will have an important bearing on other results (vide infra).

Fig. 4 shows optical storage results for a 40-bilayer sample of PAH/MA-*co*-DR13 multilayers. Note that only the first part of the curve (writing process) is shown in the figure. Two important features should be observed: first, the writing process takes much longer for dry films in comparison with films previously immersed in water. When the film is immersed into pure water for 5 min and then dried with N_2, the characteristic time—corresponding to the time to achieve 50% of maximum birefringence—drops from ~500 s (curve a) to less than 100 s (curve b). Further immersion into the water does not result in further decrease of the writing time (curve c). Second, the effect from the water on the writing properties is reversible, provided that the sample is left to rest for some days. After 4 days resting at room temperature (curve d), the sample displays basically the same behavior as before being immersed into the water (curve a). Essentially the same results are obtained with multilayer films with other numbers of bilayers (films with 20, 30, 40, and 50 bilayers were used). Chromophore aggregation is unlikely to have yielded the change in the kinetics of the writing process, since UV–vis absorption data showed that immersing the LBL films into water caused no change in the spectrum (results not shown).

One may wonder whether heating the sample could speed up the drying process. We have checked that by

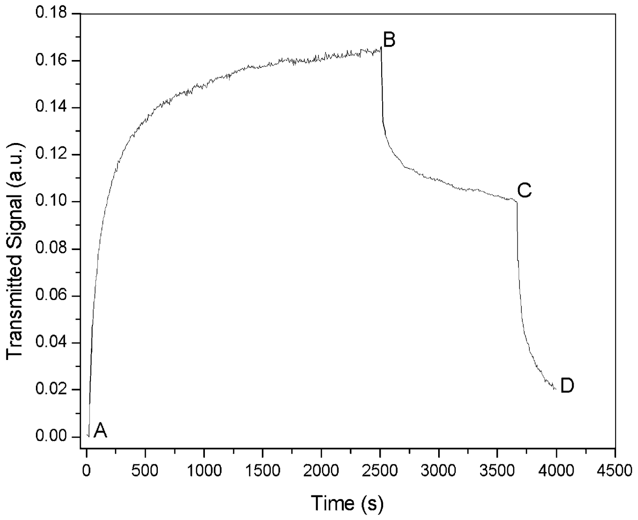

Fig. 3. Complete cycle of writing–erasure in a 40-bilayer film of PAH/MA-*co*-DR13. The linearly polarized laser was switched on at point A and switched off at point B. After allowing the sample to relax for some time, the remaining signal was erased with circularly polarized light.

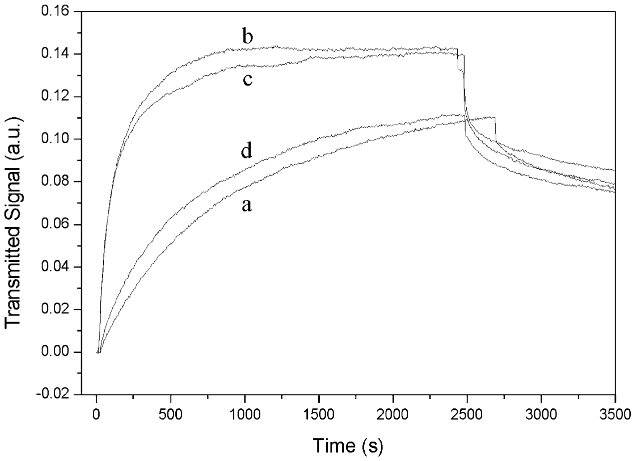

Fig. 4. Several writing processes for a 40-bilayer PAH/MA-*co*-DR13 film obtained under various conditions: (a) as-deposited film, (b) after the sample had been immersed for 5 min in water; (c) after 3 h in water; (d) the sample was left to rest for 4 days.

thermally treating LBL films at 90–100 °C for 1.5 h under vacuum and probing the photoisomerization behavior. The writing continued to be fast, and now it was not possible to revert the sample to a slow isomerization process. Even when the sample was left resting for 2 months at room temperature, as the sample used in the experiments for Fig. 4, the writing process would not become slow again. This means that the thermal treatment caused irreversible changes in the LBL film. The structure of the film is likely to have changed but this was not checked. In summary, the water effect in the optical storage properties is not reversible if the sample is thermally treated.

3.3. Mechanisms to explain the wetting effects

Two factors could be responsible for the effect from the water on the storage characteristics of the LBL films. The first and most obvious one is that the water could be acting as a plasticizer for the polymer film, causing a swelling effect and increasing the available free volume required for the molecular orientation. This would indeed cause the writing times to decrease. Since the sample was subjected to a drying procedure before the measurements, the water responsible for this phenomenon would have to be entrapped water. The morphological changes caused by exposure to humid environments have recently been investigated in monomolecular films of azobenzene-containing polymers [13], indicating that a swelling may take place. The second possibility is that the entrapped water affects the electrostatic and H-bonding interactions between the molecules in the film, in such a way that the preclusion effect brought about by such interactions on the writing processes could be diminished. The latter is in agreement with the suggestion that the interactions in LBL films may hinder photoisomerization as well as the writing of surface relief gratings [9].

In order to distinguish between the two factors, we prepared cast films from neat azopolymer MA-*co*-DR13, from MEK and from DMF solutions as well as from an aqueous solution. In addition, a cast film was prepared from an aqueous solution of the mixture of PAH and MA-*co*-DR13. The results exhibited two interesting features, as follows: first, the writing times in all cast films were considerably shorter than in the LBL films. This is illustrated in Fig. 5 for a cast film of PAH/MA-*co*-DR13 mixture from the same aqueous solutions employed to produce the LBL films of Fig. 4. Second, the writing times were not affected by immersing the samples in water, regardless of the time of immersion, also shown in Fig. 5. The same applies to the cast films of pure MA-*co*-DR13 from an aqueous solution and from a MEK/DMF solution (results not shown). The inevitable conclusion is that the swelling effect, if it exists, does not affect the orientational mechanism. It is also worth mentioning that the residual signal is lower than for the LBL films. In the latter, the electrostatic and H-bonding interactions will preclude relaxation in the same way as they preclude the writing process.

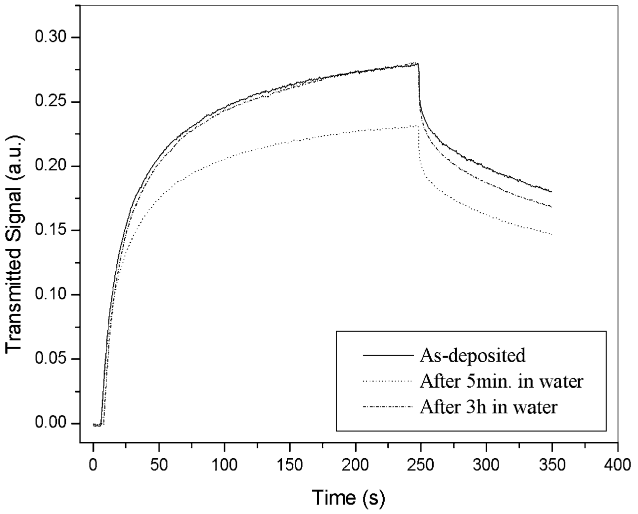

Fig. 5. Writing process for a cast film of PAH/MA-*co*-DR13 from the same aqueous solutions employed to produce the LBL films. Note that the writing time is considerably shorter than for the LBL films (Fig. 1). Immersing the sample in the water brings no significant effect.

The presence of water molecules in both LBL and cast films following immersion in water was confirmed by FTIR spectroscopy. The band between 3200 and 3500 cm^{-1} is increased for the films immersed for 3 h in water, and since the samples were dried before each measurement, the water detected must be entrapped water. This further confirms that a swelling effect is not responsible for changing the kinetics of the writing process, as the latter is only affected in the LBL layer films. Raman spectra for a 40-bilayer PAH/MA-*co*-DR13 film under two conditions; dry and after immersing in water for 5 min, are given in Fig. 6. The Raman bands and their vibrational assignments are listed in Table 1. Notably, wetting correlates with an increase in relative intensity of Raman bands originating from highly polar groups, such as NO_2 groups, that may be affected by solvation.

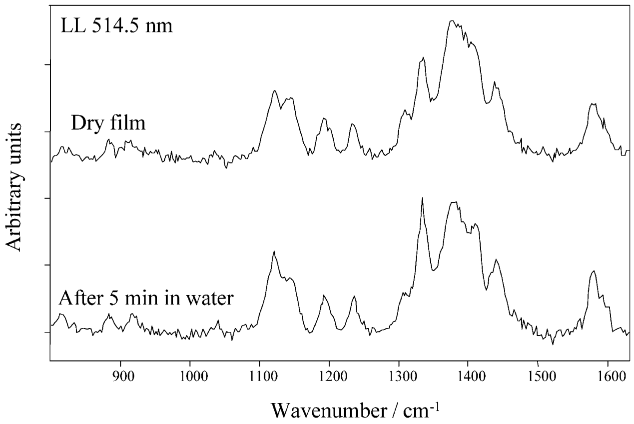

Fig. 6. Raman spectra for a 40 bilayer PAH/MA-*co*-DR13 film under two conditions: dry and after immersing in water for 5 min.

Table 1
Raman peaks and assignments for a 40-bilayer PAH/MA-*co*-DR13 film

Peak (cm^{-1})	Assignment
1120	C–O; C–N (amine salts)
1144	Aromatic ring; C–N (amine); N=N
1190	Aromatic ring and N=N
1236	CH_2 bending
1305	CH_2 bending
1332	NO_2 stretching
1390	Aromatic ring stretching; N=N
1406	Aromatic ring stretching
1440	CH_2; C=O carboxylate
1580	Aromatic ring C=C stretching

The efficiency in writing the optical information depends on two factors: (i) the ability of the chromophores to undergo *trans–cis–trans* isomerization cycles and (ii) their ability to reorient which will ultimately generate the macroscopic anisotropy in the film. While factor (ii) cannot occur without (i), the converse is not true, i.e. one may have chromophores that isomerize but are unable to reorient as this requires moving the whole polymer molecule (not only the chromophore). Obviously, some interdependence between the two factors is also expected, and it may not be possible to distinguish between them. For instance, it may be argued that if the molecule is not allowed to reorient, the attached chromophore will be locked and will not isomerize. Nevertheless, one can in principle experimentally probe isomerization independently, by measuring the fluorescence of the film upon irradiation with the appropriate wavelength. For upon absorbing energy, the chromophores may either isomerize or fluorescence, and therefore, the fluorescence intensity is a measure of the difficulty faced for isomerization.

In order to understand the effect of the water we have tried to distinguish between the two above factors using fluorescence measurements for films under various conditions. It can be seen in Fig. 7 that upon wetting a 40-bilayer film, the fluorescence decreases, which indicates that water assists in creating a more flexible environment that helps the isomerization process. However, we have also measured the fluorescence for films thermally treated at 150 °C, which showed an overall increase in fluorescence after the heat treatment. These data are omitted as they are essentially the same as in Fig. 7, except for the increase in intensity. The increase in intensity indicates that isomerization is made more difficult after the heat treatment. In spite of being more difficult to isomerize the chromophores in the treated film, optical storage measurements showed that writing is much faster after the heat treatment, and the films behave much in the same way as a cast film. Therefore, the thermal treatment most likely affected the layered structure of the film, and facilitated molecular reorientation to give origin to the anisotropy. In conclusion, even though the thermal treatment made it more difficult for the chromophores to isomerize, this is overcompensated by the greater facility for reorientation. It is postulated that the main difference between LBL and cast films—as far as the optical storage is concerned—lies in the different levels of difficulty for the molecules to reorient upon absorbing energy. The special interactions prevailing in the LBL films—ionic interactions and H-bonding—probably affect both the isomerization and the reorientation capabilities of the azobenzene chromophores, but have a larger impact on the reorientation. By the same token, incorporation of water in the LBL films certainly facilitates isomerization, but the main change in the writing kinetics for optical storage when the film is wetted must be due to the ability of water to disrupt interactions in the film that precluded molecular reorientation.

Another interesting result was obtained by blowing water vapor onto a LBL PAH/MA-*co*-DR13 film for a few seconds. Surprisingly, the sensitivity of the storage properties to the humid vapor was outstanding, as can be seen in Fig. 8 where the time to write the information was considerably shortened in comparison with an as-deposited

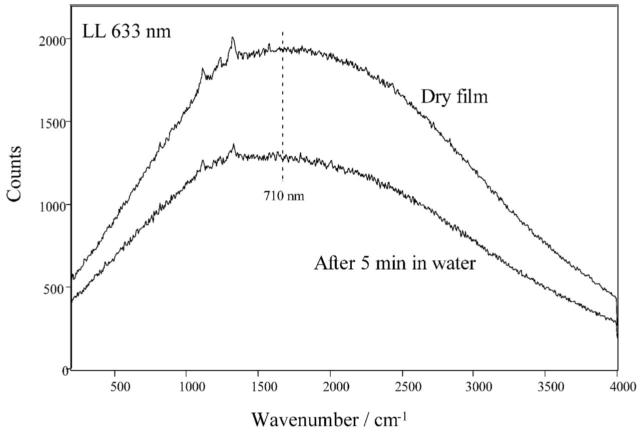

Fig. 7. Fluorescence for a 40-bilayer PAH/MA-*co*-DR13 film. Dry film and after immersing in water for 5 min.

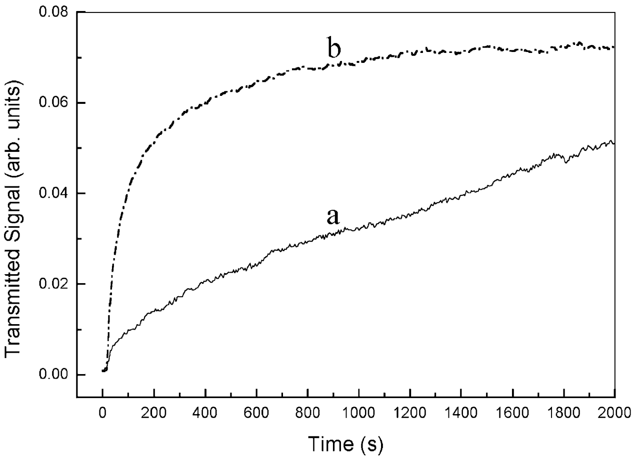

Fig. 8. Writing process on a 20-bilayer PAH/MA-*co*-DR13 film under two conditions: (a) as deposited, (b) after water vapor had been blown on the film.

film. To our knowledge this is the first demonstration of the use of photoisomerization properties (molecular orientation) of azobenzene polymers in sensing. We are now investigating if there is also selectivity for different substances in sensing.

The optical storage results presented here are entirely consistent with those reported recently by Tripathy and coworkers [9]. The latter authors not only observed that the writing times for optical storage take longer, but also that it is more difficult to write surface-relief gratings on LBL films. It is known [3,14] that the large-scale mass transport involved in the formation of surface-relief gratings requires a viscous flow that is increasingly precluded when the polymer matrix becomes rigid. This explains why writing SRGs are more difficult in high molecular weight polymers [15–17] and high T_g polymer systems [18,19]. The mass transport is, therefore, related to some type of softening (or plasticizing) of the matrix, which is induced by several photoisomerization cycles. Experimental evidence for such softening has been obtained by Srikhirin et al. [20] by measuring the elastic compliance of spin cast polymer films of polymethacrylates doped with azobenzene dyes. The electrostatic interactions in the LBL films have thus a role that is similar to increasing the rigidity of the matrix, by precluding the chromophores orientation. In our studies, the entrapped water may disrupt the electrostatic and H-bonding interactions prevailing in the LBL films, especially because of its high ability to H-bond, which cancels partially the precluding effect of such interactions in the isomerization.

4. Conclusions

The electrostatic LBL (LBL) technique was successfully employed in the fabrication of PAH/MA-*co*-DR13 films for optical storage. As expected, the writing time for LBL films was much longer than those exhibited by cast and/or LB films. This is related to the presence of strong ionic bonds and H-bonding between the film layers, which oppose molecular reorientation promoted by photoisomerization. In addition, an interesting effect was caused by water in the optical storage process, with the writing time decreasing significantly by immersing the LBL films into pure water. This effect is reversible. We have demonstrated that the water effect is not associated with swelling, but is rather due to entrapped water which affects the electrostatic and H-bonding interactions between the molecules in the film, in such a way that the mobility of the chromophores is increased.

Acknowledgments

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