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Mechanisms of surface-relief gratings formation in layer-by-layer films from azodyes

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Abstract

Surface-relief gratings are photoinscribed on ionically adsorbed layer-by-layer (LBL) films of an azodye, Brilliant Yellow (BY), which was layered alternately with a polyelectrolyte. Photoinscription is performed by impinging an interference pattern of p- or s-polarized laser light with moderate intensity onto the LBL film, which is unlikely to cause thermal effects. Large-scale mass transport occurs due to the force associated with the field gradient of the light pattern. The ionic interactions between adjacent layers appear to provide the means for the chromophores to drag the polymer chains upon photoizomerization. LBL films were produced from two different polyelectrolytes and under two distinct pH values leading to markedly different film properties especially concerning photodegradation. Exposure to the laser light, for instance, leads to higher photodegradation in the poly(dimethyl diallylammonium chloride)/BY system, in comparison to the poly(allylamine hydrochloride)/BY films. Mass transport in the latter case is predominantly light-driven, which is consistent with the higher amplitude of modulation for p-polarized light (70 nm) compared to that caused by s-polarized light (18 nm).

Keywords: Surface relief gratings; Photodegradation; Layer-by-layer

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1. Introduction

Large-scale mass transport following photoisomerization cycles in azopolymer films has been used to inscribe surface-relief gratings (SRGs) [1–4], in a process that is entirely light driven when moderate intensities of laser light are employed [5]. The formation of such SRGs can be explained with a theoretical model assuming that the molecules are moved away from illuminated regions due to the forces originating from the electric field gradient that is induced optically [6]. The forces behind this movement are a combination of the change in the susceptibility (induced by light) and the field gradient. Obviously, when large intensities are incident on the polymer film to form SRGs, thermal effects play an important role and the mechanisms for the mass transport differ [7,8]. Most studies have employed azopolymer films, in which the azochromophore is covalently attached either as a side chain or in the main chain [9]. Attempts to form gratings in guest–host systems with the azodye only physically embedded in a polymer matrix led to small surface modulations [10,11], which implies that the azochromophores need to be covalently attached to the polymer chains for the mass transport be efficient. The exception is the formation of SRGs on layer-by-layer (LBL) films, where layers of azopolymers [12] or azodyes [13] are alternated with inert polymers. In the latter case, large-scale mass transport still occurs because the ionic interaction between molecules in adjacent layers serves as the means for the chromophores to drag the inert polymer chains. Because the ionic interactions also tend to hinder photoisomerization [14], an ideal balance must be sought for the successful inscription of SRGs. The

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origin of the mechanisms is not completely elucidated, as studies with Congo Red (CR) LBL films showed that photodegradation accompanied the formation of the SRGs [13], which has been confirmed with Raman spectroscopy [15].

In this communication, we show that LBL films from another azodye, viz. Brilliant Yellow (BY), are also amenable to SRG formation. While investigating the possibility of photodegradation, we noted that LBL films with very distinct properties could be obtained upon changing some of the experimental conditions for film fabrication. In the particular case where BY is alternated with poly(allylamine hydrochloride) (PAH) at pH 10, photodegradation seems very small and SRG formation is still effective, as we shall show.

2. Experimental details

LBL films were produced from BY under two distinct sets of conditions. In the first case, BY layers were alternated with poly(dimethyl diallylammonium chloride) (PDAC). In the second, BY was alternated with PAH. PAH (weight average molecular weight (M_w) = 65,000 g/mol) and PDAC (M_w = 200,000–350,000 g/mol, 20 wt% in water) were purchased from Aldrich. BY was purchased from TCI. All the materials were used without further purification. In the PDAC/BY films the concentration of the aqueous solutions was 0.5 g/l. In the PAH/BY system, the concentration of the solutions was 0.8 and 1 g/l for PAH and BY, respectively. The anionic aqueous solution of BY was filtered with a 0.45 μm syringe filter before use. The pH of these solutions was adjusted as follows: for the PDAC/BY system, pH 7.8 and 8.0 for PDAC and BY solutions, respectively. In the PAH/BY system, all solutions had the pH adjusted to 10.0 using 1 M NaOH. The substrates were glass slides that were rendered partially hydrophilic in a 2% NaOH solution. The sequential deposition of multilayers was carried out in a HMS series programmable slide stainer (Carl Zeiss Inc.) by immersing the substrates alternately into the polycationic and anionic solutions for 10 min for each layer. After deposition of any given layer, the substrate/film system was rinsed in the washing solution. The buildup of the multilayers was monitored at each deposition step by UV–vis spectroscopy. LBL thin films of PDAC/BY and PAH/BY containing 150 bilayers were subjected to SRG inscription using a set up described in Ref. [16]. Basically, two laser beams from an Ar^+ laser at 488 nm are made to interfere on the polymer surface, thus leading to a periodically modulated intensity pattern. SRG inscription was carried out using either p- or s- polarized laser beams with an intensity of 200 mW cm^{-2}.

The Raman scattering (RS-Stokes) was obtained with a Renishaw Research Raman Microscope System RM2000 equipped with a motorized stage with a minimum step of 0.1 μm. The RM2000 uses a Leica microscope (DMLM series) and a 50 × -microscope objective was used to focus the laser beam onto a spot of ca. 1.0 μm^2. The spectrum is recorded using a Peltier cooled (−70 °C) CCD array. The Raman spectra were recorded at room temperature with ca. 4 cm^{-1} resolution. The high throughput of the instrument permits the use of very low powered lasers and 2 μW of the 780 nm laser line at the sample were used (0.2 mWcm^{-2}). The Renishaw 2000 and the 514.5 nm laser line with 4 μW at the sample (0.4 mW cm^{-2}) were used to collect the fluorescence (1 accumulation and 10 s collection time) and the pre-resonance Raman scattering (pre-RRS,10 accumulations and 1 s collection time). Data acquisition and analysis were carried out using the WiRE software for Windows and Galactic Industries GRAMS/32™ C software including the 3D package.

3. Results and discussion

The competition between ionic and secondary interactions in the adsorption processes of LBL films causes the final film properties to vary widely depending on the experimental conditions of film fabrication [17]. For the PDAC/BY films fabricated here, film growth was uniform with 28.3 Å thick bilayers being adsorbed in each deposition cycle. Fig. 1 shows the almost linear growth of the PDAC/BY and PAH/BY multilayers. The curves show the absorbance increase at the peak from the $\pi-\pi^*$ transitions of the BY (at 405 and 430 nm for the PDAC/BY and PAH/BY films, respectively). Since PDAC layers under the experimental conditions used are 10 Å thick [13], each BY layer is assumed to have a thickness of 18 Å. These films are photodegraded under UV–vis light, as illustrated in Fig. 2, for the irradiation with the 488 nm line of an Ar^+ laser where the absorbance decreases upon the irradiation. SRGs formed with such films had amplitudes of ca. 120 nm, for an interference pattern of p-polarized light of 200 mW cm^{-2} The inscription time required for saturation under these experimental conditions was ca. 45 min; however, in order

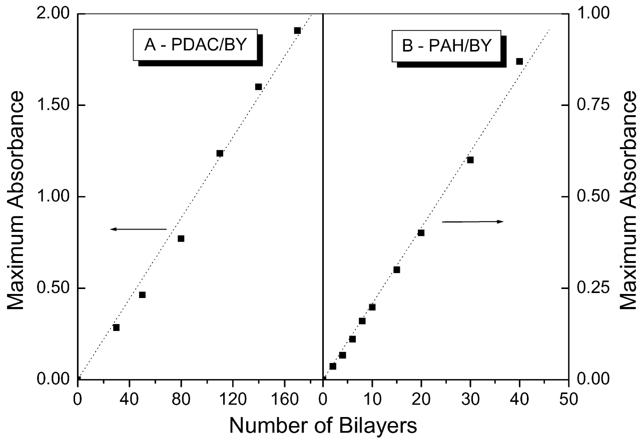

Fig. 1. Peak absorbance as a function of number of deposited bilayers for (A) PDAC/BY films and (B) PAH/BY films.

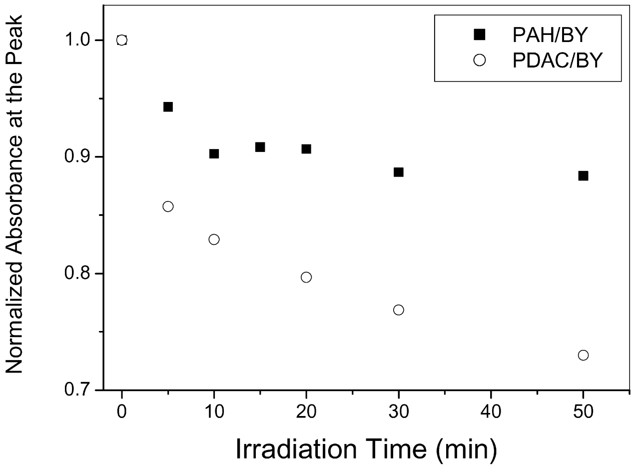

Fig. 2. Drop in the absorbance as a function of irradiation time for LBL BY films. (The samples were irradiated with a 488 nm laser light at 100 and 200 mW cm^{-2}).

to guarantee a complete inscription in all cases, the gratings were subjected to the photoinscription process for 60 min. Fig. 3 shows the AFM picture of a SRG photoinscribed on the PDAC/BY film, which shows a regularly spaced grating on a 10 × 10 μm area, in spite of the non-homogeneities of the film surface. The image is representative of several images taken over an area of 1 cm^2, which is the total area of the SRG inscribed. The irregularities in the image are due to the non-homogeneous film surface. In comparison to SRGs produced on spin-coated or cast azopolymer films, the SRG inscribed on the PDAC/BY LBL film is much shallower, thus highlighting irregularities, because the surface modulation decreases significantly when thinner films, such as the LBL films, are employed [18].

We wished to confirm whether photodegradation also occurred in the SRG inscription, and for that we employed micro-Raman spectroscopy similarly to what has been done for PDAC/CR films [15]. In the latter, an irreversible photochemical reaction occurred during the SRG inscription process in the CR/PDAC LBL films. Such photodegradation resulted in a volume collapse of the CR molecules, which contributes to the surface deformation in addition to photoinduced migration of the CR molecules in the SRG inscription process. Photodegradation was inferred by a significant decrease in the Raman peaks observed for spectra collected directly in the peak or in the valley of the SRG, in comparison to the spectra collected in a non-illuminated region of the film. Besides, an increase in the whole background was observed in the spectra for the SRG region, which was attributed to the presence of degraded carbon [15]. The presence of photodegraded material in the PDAC/CR films was also observed via UV–vis and FT-Raman spectroscopies [13].

The pre-RRS spectra of PDAC/BY film collected from selected spatial regions of the grating using the 514.5 nm laser line are shown in Fig. 4. The Raman peaks from BY in the SRG regions are observed with a poorer signal-to-noise ratio, but the relative intensities among peaks are the same as outside the SRG. Furthermore, the difference in the fluorescence spectra (Fig. 5) collected from regions inside and outside of SRG was small-though not negligible. The small decrease in fluorescence is consistent with a low level of photodegradation in the SRG, considerably lower than for the SRGs on CR films [15]. This low level of degradation prompted us to further investigate the possibility of producing degradation-free SRGs in LBL films from BY.

LBL systems presenting very small photodegradation were found when PAH/BY films were fabricated from high pH dipping solutions. The actual measurements corresponding to the UV–vis absorption spectroscopy are presented in Fig. 2 in solid squares. The photodegradation is considerably smaller than that observed for PDAC/BY films (open circles) and could not be detected in the Raman scattering from regions containing SRGs. Fig. 6 shows that the spectra are essentially the same for three regions of a BY/PAH film. Notably, the signal-to-noise ratio is practically identical for all three spatial regions. The fact that low level of photodegradation was observed in the SRG film inscription via UV–vis spectroscopy but not in micro-Raman spectroscopy is not surprising. The photodegraded material has

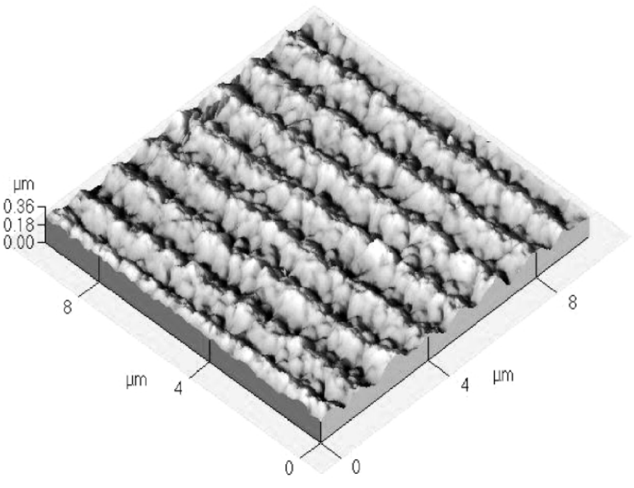

Fig. 3. AFM image of an SRG inscribed on a 150-bilayer PDAC/BY film.

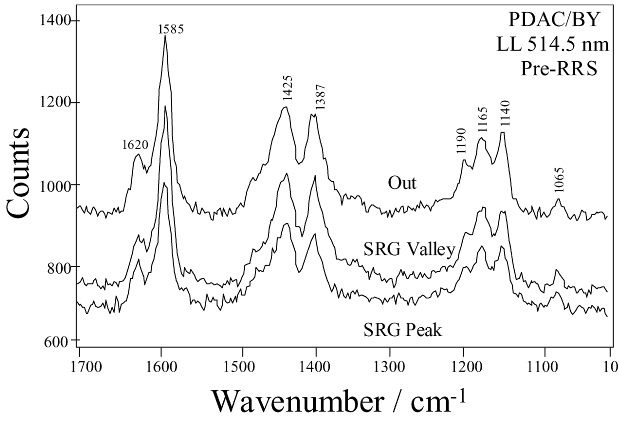

Fig. 4. Pre-RRS for three regions of a PDAC/BY film: peak of the SRG, valley of the SRG and outside the SRG, as indicated.

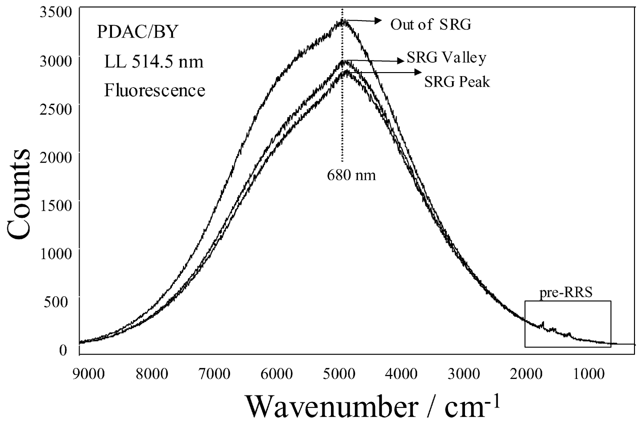

Fig. 5. Fluorescence spectra recorded from regions inside and outside of SRG using the 514.5 nm laser line.

smaller Raman scattering cross section as the laser line is not near-resonant and mainly contributes to the background signal. Therefore, a decrease in the electronic absorption measurements would be followed by a corresponding decrease in the absolute intensity of the Raman signal, which in our case translates into a lower signal-to-noise ratio. The differences between the BY/PDAC and BY/PAH films are believed to be associated with distinct electrostatic and molecular interactions occurring in the films, which is also the reason why the pH-dependence for film thickness (per layer) and level of interpenetration varies in LBL films from PDAC or PAH alternated with polyelectrolytes [19, 20]. Since PDAC is a strong polyelectrolyte, the amount of charge in the chain does not vary with pH, whereas a strong pH dependence occurs for PAH.

With low level of degradation and with the moderate laser intensities used, it is reasonable to wonder whether the mechanism for large-scale mass transport is the same as in spin-coated films of azopolymers. If so, the field-gradient model [6] should be applicable. The easiest way to test the validity of the model is to investigate the polarization dependence of the SRG formation. As is well established, significant surface modulation is only achieved when there is a component of the electric field gradient in the direction of the grating vector, which means that s-polarized light should lead to no SRG. The AFM pictures in Fig. 7 show the SRGs recorded using either p- and s-polarized light. The amplitude of the SRG obtained with the p-polarized light is 3.9 times the amplitude found for the s-polarized light (an average value of the amplitudes was 70 nm for polarization p and 18 nm for polarization s). Such ratio of amplitudes is consistent with a more efficient SRG formation for the p-polarized light, whereas for the CR/PDAC films the SRG amplitude for the p-polarized light was only twice the value of that obtained with s-polarized light [13,15]. Nevertheless, the amplitude of the SRG with s-polarized light for BY/PDAC films was not negligible, contrary to the prediction of

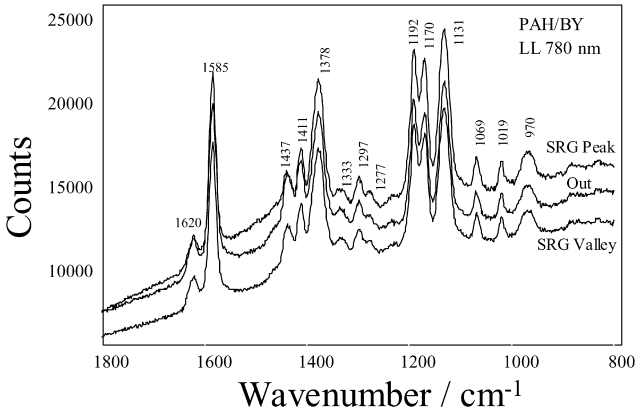

Fig. 6. RS for three regions of a PAH/BY film: peak of the SRG, valley of the SRG and outside the SRG, as indicated.

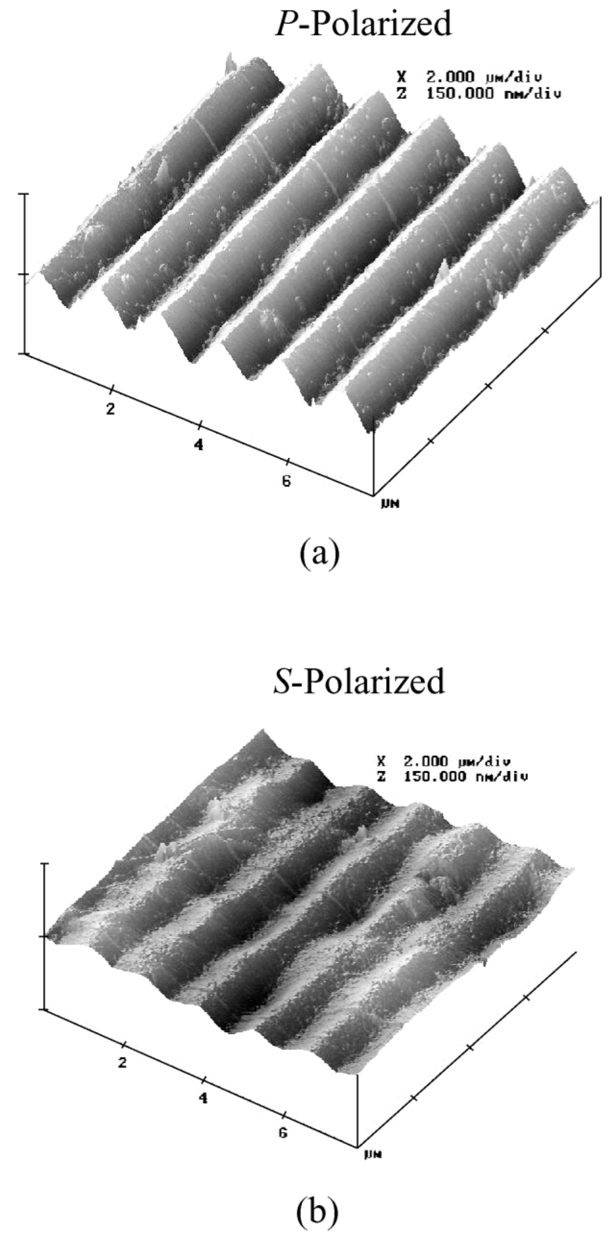

Fig. 7. AFM images of SRG on PAH/BY films: (a) SRG inscribed using two p-polarized laser beams and (b) using two s-polarized laser beams.

the theoretical model. This confirms that photodegradation may still affect the mass transport leading to the SRG, but not as strong as with other systems [13].

4. Conclusions

In summary, we showed that SRGs can be photoinscribed on LBL films of the azodye BY, similarly to what was observed for CR. The degree of photodegradation depends on the procedures adopted and the polyelectrolytes used to fabricate the films. The mechanism for the SRG formation is mostly the light-driven large-scale mass transport, as in the spin-coated films of azopolymers. The electrostatic interactions are important for mass transport leading to the formation of SRG. These interactions effectively connect the dyes to the polymer allowing the photocycled azo dyes to drag the non-absorbing polymer chains.

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