Analysis of Wavelength Effect on Birefringence Creation on PAH/PAZO Layer-by-Layer Films

Maria Raposo[a], Ana Rita Monteiro Timóteo and Paulo António Ribeiro[b]
CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, UNL, Campus de Caparica, 2829-516, Caparica, Portugal

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Abstract: The influence of wavelength of writing laser beam in the photoinduced birefringence dynamics on layer-by-layer (LBL) films of poly(allylamine hydrochloride) (PAH) and poly{1-(4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido)-1,2-ethanediyl, sodium salt} (PAZO) was investigated. Results revealed that the increase of laser wavelength lead to a slower birefringence build up process, whereas the relaxation process stands approximately unchanged. The buildup celerity was shown to follow the film absorbance with wavelength. The imposition of excess energy density to the PAH/PAZO LBL film was also shown to induce morphological changes in the film surface,which are also wavelength dependent.

1 INTRODUCTION

Polymeric materials containing azo-chromophores have been shown suitable for the development of optical storage devices, sensors, polarization holography and programmable lenses, which mainly arises from the irreversible anisotropy capabilities, see for example (Mysliwiec, 2007), (Shinbo, 2002), (Buffeteau, 2004), (Monteiro Timóteo, 2016), (Chaganava, 2018) and references therein. These result from the photo-isomerization features about the N=N group of the azo-chromophore(Barrett,1994). As consequence, a net birefringence can be created in these materials just by irradiation with polarized light of adequate wavelength. This net birefringence attained in the medium is due to the alignment of azo-chromophores in a direction normal to that of the applied optical electric film, as a result of multiple *trans–cis–trans* photoisomerization cycles..

Although, in the traditional experiments, high power laser beams are used to induce birefringence in these materials, light coming from halogen lamp bulb was also shown to be able to induce a small birefringence in azo-benzene chromophore containing thin films, in a direction parallel to its surface (Farinha, 2016) and (Zagalo, 2017). This result creates expectations for the use of azobenzene containing materials in the development of energy harvesting devices.

In this work, the effect of light wavelength, in the visible region, on the dynamics of birefringence creation in layer-by-layer (LbL) of the common polyelectrolyte (PAH) and the azo-polyelectrolyte poly{1-(4-(3-carboxy- 4-hydroxy phenylazo) benzene-sulfonamido)- 1,2-ethanediyl, sodium salt} (PAZO).

2 EXPERIMENTAL DETAILS

The LbL films used in this work were prepared from 10^{-2} M solutions of PAH and PAZO, obtained by dissolving each of the polyelectrolytes in Milli-Q ultrapure water, supplied by Millipore (resistivity 18 MΩ.cm at 25ºC). The pH of PAZO and PAH solutions was set to 7 and 5, respectively. The PAH/PAZO LBL films were built onto BK7 optical glass substrates which were previously hydrophilized according with procedure described by (Monteiro Timóteo, 2016). The film production procedure consists of the alternated adsorption from the respective solutions of both polyelectrolytes and

[a] https://orcid.org/0000-0003-4710-0693
[b] https://orcid.org/0000-0001-9665-7610

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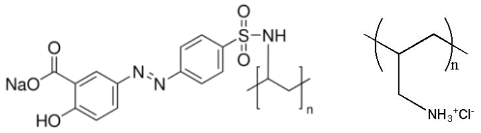
comprehends the following sequence: (a) immersion of the substrate in the PAH solution for 3 minutes; (b) washing the substrate, with one layer adsorbed, in ultrapure water; (c) immersion of the substrate with one layer in the PAZO solution for 3 minutes; (d) washing the substrate, with one bilayer adsorbed, in ultrapure water. Repeating this process ten times leads to ten bilayers PAH/PAZO LbL films $(PAH/PAZO)_{10}$, to be used in this work.



a) b)

Figure 1: Schema of the molecular structure of: a) PAZO and b) PAH polyelectrolytes.

The birefringence dynamics was obtained using a two nearly collinear laser beams setup intersecting each other at the sample surface. The laser beam of tuneable Ar^+ laser was used to induce birefringence in the films (the writing beam), while a low-power He-Ne laser was used as a probe beam to measure birefringence. The sample was placed between crossed polarizers with respect to the probe beam, so a maximum sensitivity can be achieved. The probe beam was modulated by means of an optical chopper in order to minimize the optical noise originated from ambient light. In this way the birefringence signal at the modulation frequency was measured with a photodetector through a lock-in amplifier. The kinetic birefringence curves were obtained at the fixed power of 10 mW and at different wavelengths of writing laser beam.

Film surface optical images were obtained in a Nikon Eclipse LV100 microscope.

3 RESULTS

To study the effect of wavelength of the writing laser beam, the birefringence buildup kinetic curves were obtained for different writing laser wavelength values, at the fixed laser beam power of 10 mW, corresponding to a light intensity of 141 $mW \cdot cm^{-2}$. The obtained birefringence creation curves are shown in Figure 2. The birefringence buildup characteristic times and the magnitudes of the involved processes were calculated from fitting the experimental data to the equation:

$$I_w = I_{w1}\left(1 - exp\left(-\frac{t}{\tau_{w1}}\right)\right) + I_{w2}\left(1 - exp\left(-\frac{t}{\tau_{w2}}\right)\right) \quad (1)$$

where I_{w1} and I_{w2} are pre-exponential factors that represent the magnitude of each process, and τ_{w1} and τ_{w2} are the fast and slow processes characteristic time constants. Normally a faster and a slower process is observed, with the fast process usually assigned to the *trans→cis→trans* photoisomerization cycles, which are dependent on the free local volume and interactions between chromophores and PAH polyelectrolyte; while the slower process, is normally attributed to the chain mobility, which relies on the size of the chain and interactions between both electrolytes (Ferreira, 2012).

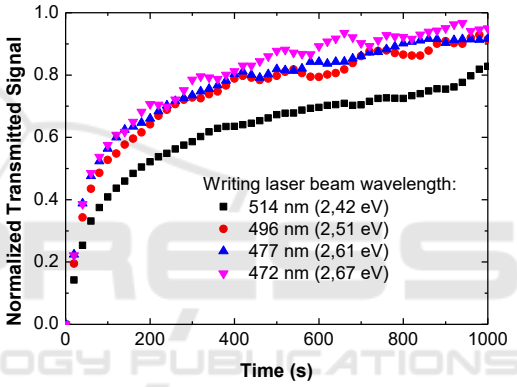


Figure 2: Birefringence creation kinetic curves for a variable writing laser beam wavelength and at a fixed power of 10 mW.

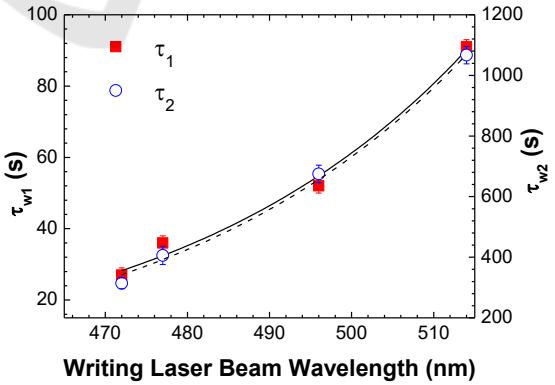


Figure 3: Fast and slow characteristic time constants versus writing laser beam wavelength values.

The calculated normalized magnitudes of both fast and slow processes revealed to be practically constant, for the different writing laser beam

wavelengths. Mean values of normalized magnitudes of 0.51 ± 0.03 and 0.49 ± 0.03 were obtained for the fast and slow processes relative magnitudes, respectively. This allows concluding that the laser wavelength is not influencing the amount of chromophores which are being orientated as a result of *trans→cis→trans* photoisomerization cycles and resultant molecular reorientation. Thus it can be inferred that the process celerity should be related with changes in the film free volume, as the molecular reorientation strongly depends upon it. The buildup process turns slower with the increase in laser beam wavelength increase, once the characteristic times are seen to increase, as shown in plot of Figure 3. From this figure one can also notice that both fast and slow processes follow the same trend although with effective values completely distinct.

From a different perspective, at wavelengths close to that of the azo group maximum absorbance, which in the present case is of 360 nm (Ferreira, 2013a and 2013b) smallest characteristic times values are expected, since the birefringence is more effectively induced in the region of the absorption band. The fast process speed constants or rate constants were calculated and plotted as a function of wavelength, together with the film absorbance values. These plots, presented in Figure 4, allow conclude that the process celerity is in fact related with the film absorbance.

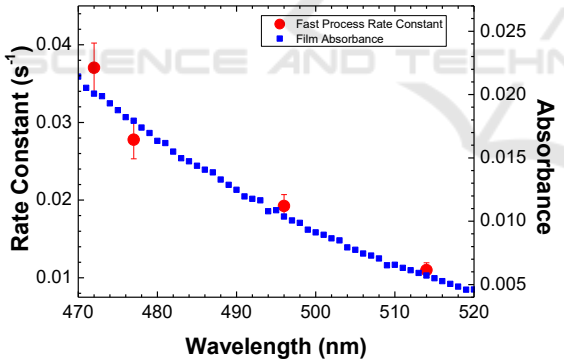


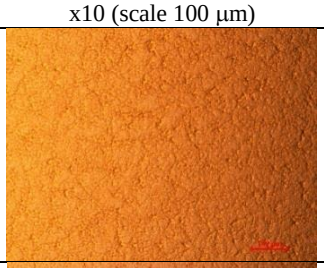
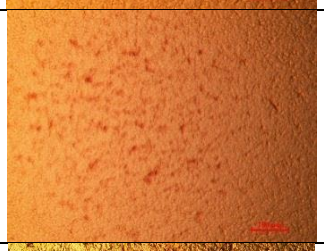
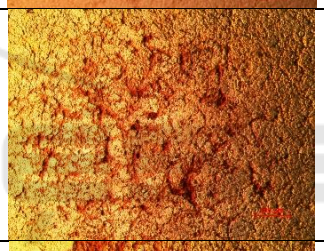
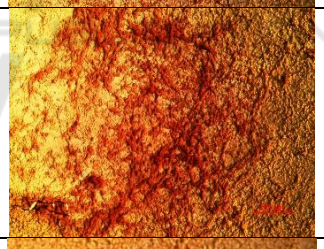
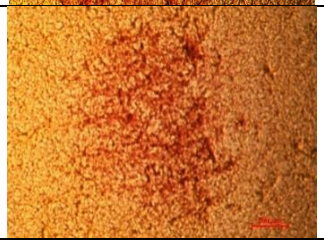
Figure 4: Relation between the buildup process celerity and the $(PAH/PAZO)_{10}$ film absorbance.

The relaxation curves were also acquired after turning off the Ar^+ laser, data not shown here, and the respective data were fitted with the equation:

$$I_r = I_{r1} exp\left(-\frac{t}{\tau_{r1}}\right) + I_C \qquad (2)$$

where I_{r1} is the pre-exponential factors for the birefringence normalized intensity, τ_{r1} is the characteristic time constant of the process and I_C represents the long-term relaxation. Results revealed that the relaxation process seems to be independent of the irradiation wavelength, presenting characteristic time of 249 ± 76 s. This characteristic time reveals that the relaxation process strongly depends on the azopolymer intrinsic properties, an effect that can be only thermally dissipated.

Table 1: Images obtained by optical microscopy, in bright Field contrast mode, in the irradiated spot region, corresponding to $(PAH/PAZO)_{10}$ LbL films irradiated at different wavelengths. The non-irradiated region of the film is also presented for comparison. The images presented were obtained with x10 magnification lenses.

λ(nm)	x10 (scale 100 μm)
---	
514	
496	
477	
465	

In order to investigate possible effects caused by exposure to the writing laser beam, the films were analysed under an optical microscope after being

subjected to the high irradiation times. The obtained surface images are shown in Table 1, together with respective irradiations wavelengths.

The images of the affected area of the film revealed morphological changes compared to a similar non irradiated film. It can also be observed that the intensity of the observed morphological changes increases with the energy of the incident beam, that is, the more energetic the incident radiation used, the greater are resulting surface effects.

4 CONCLUSIONS

The wavelength of writing laser was shown to contribute to the birefringence creation processes in $(PAH/PAZO)_{10}$ LBL films, with higher wavelengths imposing a decrease in the birefringence buildup kinetics. This behaviour can be attributed to the fact that for wavelengths far from the azo group resonance wavelength (360 nm), the films absorbance is smaller which means less energy uptake from laser beam. In addition, the buildup celerity was shown to follow the film absorbance change with wavelength. The irradiation of PAH/PAZO LBL films of with an excessive dose of radiation, allowed to deduce that the greater the energy of the radiation the less the fluency, that is to say, the smaller the density of energy that the film "accepts". The imposition of excess energy density to the PAH/PAZO LBL films was also shown to induce morphological changes in the surface of PAZO films which are also seen to be wavelength dependent.

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