

Electric-field Induced Birefringence in Azobenzene Thin Films

Paulo M. Zagalo, Gonçalo Magalhães-Mota, Susana Sérgio, Paulo A. Ribeiro and Maria Raposo
*CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, UNL,
Campus de Caparica, 2829-516 Caparica, Portugal*

Keywords: Birefringence, Azobenzene, PAZO, Thin Films, Energy Harvesting.

Abstract: It has been recently shown that solar light is able to induce a small birefringence in azo-benzene chromophore containing thin films, parallel to its surface. In order to enhance this effect, towards the development of energy harvesting devices, poly{1-(4-(3-carboxy-4-hydroxy-phenylazo)benzenesulfonamido)-1,2-ethanediyl, sodium salt} (PAZO) cast films were thermally polarized to achieve a net dipole moment in the medium. Therefore, creation and relaxation kinetics curves of PAZO cast films were obtained in terms of poling at different temperatures and applied voltages. Results show that the maximum birefringence induced is proportional to both temperature and applied external electrical field while the relaxation curves reveal that the residual birefringence increases with the temperature, behaviour which is indicative of cooperative orientation processes between the chromophores which in turn guarantees the stability of chromophores orientation.

1 INTRODUCTION

The growing requirements for optical signal processing in current optical fibre based telecommunications is seeking for the development of novel photonic devices, capable of processing optical signals, towards higher processing rates capabilities and lower energy consumption. Among other functionalities of interest to be addressed are light modulation, optical amplification, optical multiplexing/ demultiplexing, optical selective filtering, optical storage and energy harvesting, all to be integrated in an all-optical based architecture.

The development of novel optical devices for integrated optics requires the addressing of both novel materials and material processing procedures. Photonic materials of particular interest are those containing highly polarizable chromophore molecules. Among these the azo-benzene based chromophores have been arousing much attention from the scientific community as a result of their photochromic features. These are formed by a pair of benzene rings chemically bound together via two double bonded nitrogen atoms and having a donor group in one of the benzene ring and an acceptor on the other. The main interest for the azo-chromophores comes from their photoisomerization capabilities which induces spatial rearrangement of the

chromophore molecules, as result of trans-cis-trans conformation interchange (Hartley, 1937) (Natansohn and Rochon, 2002). This process under certain light conditions, light wavelength and polarization state, can give rise to anisotropy creation within the medium containing the azo-chromophores and results in a net birefringence (Kasap, 2013). This feature can be of particular interest for the creation of energy harvesting devices, based on the photoelectret concept (Farinha, 2016). These devices consist of a medium having oriented dipoles, thus with a net polarization, which can be changed by an external stimulus, in a process that can give to the delivery of electrical current to an external circuit. Changes in device polarization can be achieved either by mechanical stress, temperature, chemical reaction, or in the case of photoisomerizable azochromophores by light. For device production, generally the azochromophores are incorporated in a polymeric matrix and processed in electrode thin film form. The orientation of electrical dipoles can be achieved by optical poling or by the application of an external electric field at temperatures close to that of the glass transition temperature and then cooled down to room temperature with the electrical field applied.

In this work the birefringence induced by external poling electric field will be investigated in thin films of the azo-polymer poly{1-(4-(3-carboxy-4-hydroxy-

phenylazo) benzenesulfonamido)-1,2-ethanediyl, sodium salt} (PAZO) in terms of poling temperature and polarization voltage, having in view its use in energy harvesting devices.

2 EXPERIMENTAL

2.1 Materials and Methods

Poly{1-(4-(3-carboxy-4-hydroxy-phenylazo)benzene sulfonamido)-1,2-ethanediyl, sodium salt} (PAZO), figure 1, was acquired from Sigma Aldrich. Cast films of PAZO were prepared by spilling drops of PAZO solution with 10^{-2} M concentration using methanol as solvent onto BK7 glass substrates with two regions of FTO 1 mm apart. For this, glass supports with a FTO layer with a thickness of 414 ± 6 nm were used, and, in the middle, a 1 mm strip of FTO was removed from the glass support by depositing a mash of zinc metallic powder with a few droplets of hydrochloric acid on it. The cast films were then dried by leaving the solid supports with PAZO solution in a desiccator for about two hours.

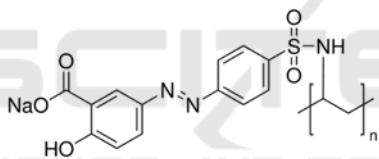


Figure 1: Chemical structure of the PAZO.

2.2 Birefringence Measurements

The samples were placed in a sample holder with heating facilities and two electrical spring metallic probes were used to connect the FTO electrodes with a high voltage power supply HCN14 (0-20 kV) for sample poling. The spring probes were placed in contact with the opposite ends of the FTO conducting surfaces. A laser beam was then made go impinge the sample, in the gap between electrodes, and hit a photodetector that was connected to a National Instruments SCB-68 tracer. The sample was placed between crossed polarizers, as depicted in Figure 2 (Monteiro-Timóteo, 2016). The laser and photodetector used were a Melles Griot with 6,35 mW and 632.8 nm and a Newport Corporation 818-UV/DB (200-1100 nm), respectively. The samples were heated to different temperatures while keeping the electric field applied. Under these conditions, the transmitted signal intensity can be related to birefringence by the expression:

$$\Delta n = \frac{\lambda}{\pi l} \sin \sqrt{\frac{I}{I_0}} \quad (1)$$

where λ is the wavelength of the probe beam, l the film thickness, I_0 the incident beam intensity, and I the intensity after the analyzer. The transmitted light through crossed polarizers reaching the photodetector was monitored during polarization process and during polarization relaxation after electrical field removal.

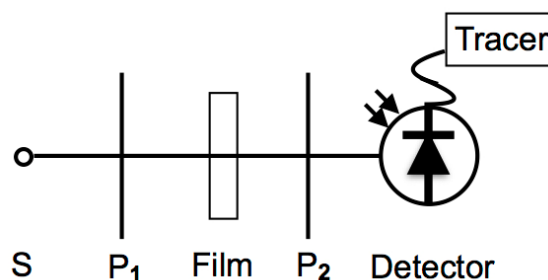


Figure 2: Schematic of the configuration implemented to measure the birefringence in the films.

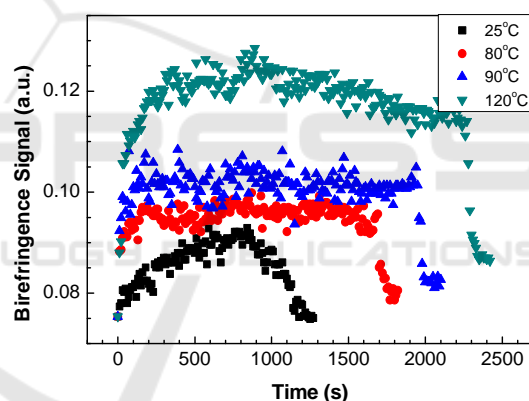


Figure 3: Birefringence creation and relaxation kinetics curve at room temperature obtained in PAZO cast films with a voltage of 600V applied.

3 RESULTS AND DISCUSSION

The birefringence creation and relaxation kinetics curves obtained for PAZO cast films are shown in Figure 3. The birefringence creation curves correspond to the increase of transmitted light signal until the applied voltage of 600V be turned off; while the birefringence relaxation curve is obtained immediately after the voltage be turned off and corresponds to a decrease of the transmitted signal. The obtained curves present a similar behaviour of the photoinduced birefringence build-up (Ferreira, 2007) (Ferreira, 2012), increasing the value of

birefringence with the time of application of the electrical field.

The photoinduced birefringence creation kinetics curves can be analysed fitting the experimental data to a sum of two exponential functions, which indicates the presence of two distinct processes in accordance with literature (Ferreira, 2012). One of these process is a fast process usually assigned to the birefringence induced by instantaneous polarization, which depends on the free local volume available and on interactions between chromophores. While the second is a slower process attributed to the main chain mobility, which relies on chain size and interactions between polymeric chains. In the present case, the birefringence creation, $I_{writing}$, is relatively slow so that the experimental data can be fitted by a single exponential function:

$$I_{writing} = I_{w0} \left(1 - \exp\left(-\frac{t}{\tau_w}\right) \right) \quad (2)$$

where I_{w0} is the pre-exponential factor that represents the magnitude of the process and τ_w is the characteristic time constant. The values of writing characteristic times obtained from birefringence induced by electrical field are displayed in table 1. The activation energy calculated from these values, using the method described by (Ferreira, 2012), takes a value of $53 \pm 3 \text{ kJ/mol}$.

Table 1: Writing and relaxation characteristic times obtained from fitting of curves of figure 3.

Temperature (°C)	τ_w (s)	τ_{r1} (s)
25	670 ± 80	88 ± 7
80	20 ± 1	36 ± 2
90	18 ± 1	24 ± 1
120	3.5 ± 0.5	31 ± 1

From the obtained birefringence creation curves one can observe that the induced birefringence increases, as temperature increases. Opposite results have been obtained by Ferreira et al (Ferreira, 2012) in poly(allylamine hydrochloride) (PAH)/PAZO Layer-by-Layer (LbL) films when irradiated with the 488 and 514 nm lines of a tunable Ar^+ laser, used as writing beams for inducing birefringence. In fact, it has been shown that birefringence decreases linearly with the increase of temperature. For the present case, the maximum attained birefringence increases linearly with temperature, as can be seen in graph of figure 4, which indicates that the temperature promotes dipolar orientation.

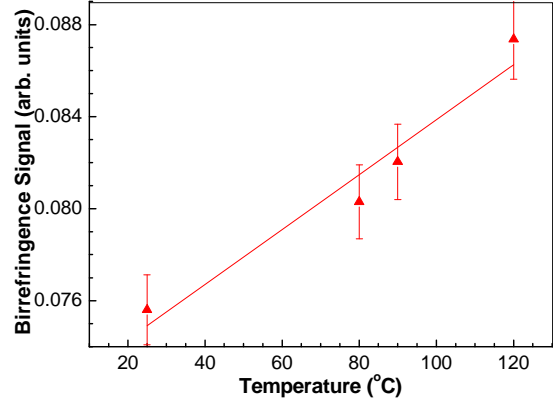


Figure 4: Maximum intensity of birefringence for PAZO cast films attained at different temperatures with a constant voltage of 600V applied.

The birefringence decay curves can be fitted with two exponential Debye like processes as follows:

$$I_{relaxation} = I_{r1} \exp\left(-\frac{t}{\tau_{r1}}\right) + I_{r2} \exp\left(-\frac{t}{\tau_{r2}}\right) \quad (3)$$

where I_{r1} and I_{r2} are the pre-exponential factors for the birefringence normalized intensity, τ_{r1} and τ_{r2} are the characteristic time constants of the processes. The process with shorter characteristic time is usually associated with dipole disorientation and the one with longer characteristic time the long-term relaxation related to disorientation arising from the movement of polymer chains. In the present case, the second process revealed to be slow enough so that the relaxation kinetics curves were fitted with an exponential decay curve plus a constant. The relaxation characteristics are also displayed in table 2.

It should be also worth to refer that the residual birefringence after the relaxation of orientated chromophores, which follows the fast relaxation process, increases as the temperature increases as shown in graph figure 5, where the residual birefringence signal is plotted as a function of temperature. This result indicates that temperature promotes the chromophores orientation and the alignment is contributing to the cooperative aggregation which was proven to be more effective in accordance with photoinduced birefringence results obtained in PAH/PAZO LbL films (Ferreira, 2012). It should be also referred that the calculated value of activation energy of $53 \pm 3 \text{ kJ/mol}$ is very close of the value obtained by (Ferreira, 2012) for PAH/PAZO LbL films prepared with $\text{pH}=8$ and where it was

proved that cooperative aggregation has a major contribution.

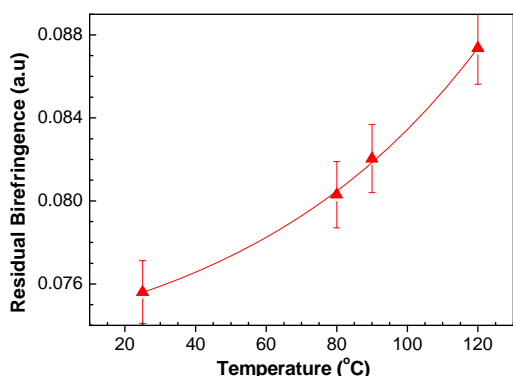


Figure 5: Residual birefringence after the fast relaxational process for PAZO cast films firstly subjected at different temperatures with a constant voltage of 600V applied. The solid line is a guideline.

Figure 6 shows the birefringence creation and relaxation kinetics curves obtained for PAZO cast films by applying different poling voltages, while maintaining the temperature constant at 120°C. From these results, one can conclude that the induced birefringence increases with the applied electrical field established in the gap between electrodes.

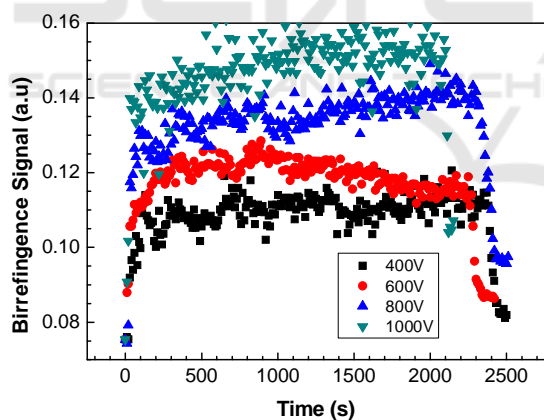


Figure 6: Birefringence creation and relaxation kinetics curve at room temperature obtained in PAZO cast films with different voltages applied. The temperature was maintained constant at 120°C.

By plotting the maximum birefringence attained versus the applied voltage, as shown in figure 7 one can conclude that induced birefringence is proportional to the applied external electrical field. These results show that it possible to orientate the chromophore of the PAZO molecules and to create a net birefringence in the medium by applying an

external electrical field. If the medium is now subjected to polarized light, one expects that azochromophores will be able to experience successive cis-trans-cis processes, which induce changes in sample dipole moment and thus can deliver current to an external circuit.

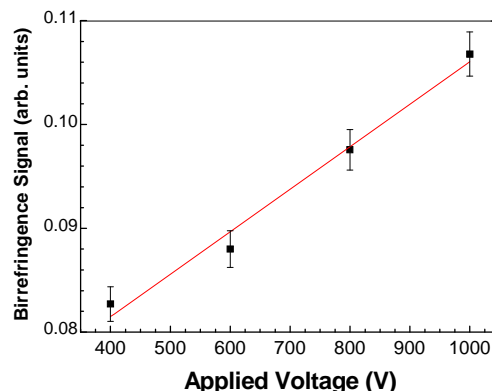


Figure 7: Maximum intensity of birefringence for PAZO cast films attained with different voltages applied. The temperature was maintained constant at 120°C.

4 CONCLUSIONS

This work demonstrates that birefringence can be induced in PAZO cast films by electrical poling close the glass transition temperature. The birefringence kinetics curves revealed that the maximum birefringence induced is proportional to both temperature and applied electrical field. Moreover, the obtained values of characteristic times of birefringence creation and relaxation kinetics curves are strongly dependent of temperature, allowing to conclude the poling process is much more effective at high temperatures and high applied voltage. The relaxation curves reveals that the residual birefringence also increases with temperature which indicates that cooperative processes between the chromophores are taking place in such a way that guarantees the stability of chromophores orientation. One expects that after electrical poling, if the medium is subjected to polarized light, more azochromophores are now be able to experience successive cis-trans-cis processes, which induce changes in sample dipole moment and thus can deliver current to an external circuit.

ACKNOWLEDGEMENTS

This work was supported by the Portuguese research

Grant UID/FIS/00068/2013 through FCT-MEC, the "Plurianual" financial contribution of "Fundação para a Ciência e Tecnologia" (Portugal) and by the project POCTI/FAT/47529/2002 (Portugal).

REFERENCES

- Farinha, P., Sérgio, S., Ribeiro, P.A., Raposo, M., 2016. Birefringence Creation by Solar Light - A New Approach to the Development of Solar Cells with Azobenzene Materials, In Proceedings of the 4th International Conference on Photonics, Optics and Laser Technology (PHOTOPTICS 2016), 365-368.
- Ferreira, Q., P. J. Gomes, M. Raposo, J. A. Giacometti, O. N. Oliveira Jr. P. A. Ribeiro, 2007 a. Influence of Ionic Interactions on the Photoinduced Birefringence of Poly[1-[4-(3-Carboxy-4 Hydroxyphenylazo) Benzene Sulfonamido]-1,2-Ethanediy], Sodium Salt] Films, *J. Nanosci. Nanotechnol.* 7, 2659–2666.
- Ferreira, Q., Ribeiro, P.A., Oliveira Jr., O. N., Raposo, M., 2012. Long-term stability at high temperatures for birefringence in PAZO/PAH layer-by-layer films, *ACS Applied Materials and Interfaces*, 4, 1470-1477.
- Hartley, G. S.; 1937. The cis-form of azobenzene, *Nature*, 140, 281.
- Kasap. S.O., 2013. Optoelectronics and Photonics: Principles and Practices. Pearson Education Limited, 2nd edition.
- Monteiro Timóteo, A.M, Ribeiro, J. H.F., Ribeiro, P.A., Raposo, M., 2016. Dynamics of creation photoinduced birefringence on (PAH/PAZO)_n layer-by-layer films: Analysis of consecutive cycles. *Optical Materials* 51, 18–23.
- Natansohn, A., Rochon, P., 2002, Photoinduced Motions in Azo-Containing Polymers. *Chem. Rev.* 102, 4139–4175.