

# Optical, electrical, and thermochromic properties of polyazothiophene Langmuir–Blodgett films

Vanessa C. Gonçalves · Marystela Ferreira ·  
Clarissa A. Olivati · Marcos R. Cardoso ·  
Cleber R. Mendonça · Debora T. Balogh

Received: 2 April 2008 / Revised: 30 June 2008 / Accepted: 3 July 2008 / Published online: 7 August 2008  
© Springer-Verlag 2008

**Abstract** The conductivity and luminescence of conjugated polymers may be combined with the photoisomerization capability of azobenzene materials to achieve unique properties for a variety of applications, particularly if conjugated polymers with azobenzene side chains are processed as nanostructured films. In this study, we report on Langmuir–Blodgett (LB) films of a polythiophene-bearing azobenzene moieties, which displayed photoluminescence, thermochromism, electroactivity, and photoinduced birefringence. The latter three properties were enhanced in the LB films, as compared to spin-coated films of the polyazothiophene, and this has been attributed to differences in film morphology that could be probed with atomic force microscopy.

**Keywords** Langmuir–Blodgett · Polythiophenes · Azobenzene

## Introduction

The azobenzene chromophore is a photoisomerizable moiety used in applications such as reversible optical data storage, surface relief gratings, and electro-optic devices [1–5]. Polythiophenes are conducting polymers with good thermal and environmental stability, being easier to functionalize than other conjugated polymers [6, 7]. The combination of the polythiophene backbone with side-chain azobenzene moieties, in the so-called polyazothiophenes, can impart unique properties to these new materials with various potential applications. Polythiophenes with different types of azobenzene linked to the polymer backbone as side chain have been synthesized [6–18], which displayed different types of chromism, namely thermochromism in solutions and films, solvatochromism, electrochromism, and photochromism [16–18]. The photoinduced birefringence of polyazothiophene thin films was studied by Aubertin et al., but only a small anisotropy was achieved under the conditions used [15].

One important issue in the evaluation of new materials for optical applications is the possibility to control the molecular structure in the films. Conventional film-forming techniques to produce polymeric films from solutions, such as casting and/or spin-coating, do not offer thickness control. Nanostructured films with high control of film thickness and uniformity have been obtained by techniques such as Layer-by-Layer [19] and Langmuir–Blodgett (LB) [20]. For some materials, thin films made with these techniques exhibited an anisotropy inherent in the deposition method [21, 22]. In an earlier study [23], we reported chromic properties of a polyazothiophene in solution, including thermochromism in different solvents and concentrations, solvatochromism, and halochromism. Here, we explore the thermochromism, electrochemical response, and

---

V. C. Gonçalves · M. R. Cardoso · C. R. Mendonça ·  
D. T. Balogh (✉)  
Instituto de Física de São Carlos, USP,  
CP 369,  
13560-970 São Carlos, SP, Brazil  
e-mail: balogh@ifsc.usp.br

M. Ferreira  
Campus de Sorocaba-Rodovia João Leme dos Santos SP 264,  
Universidade Federal de São Carlos,  
Km 110 CP 3031,  
18043-970 Sorocaba, São Paulo, Brasil

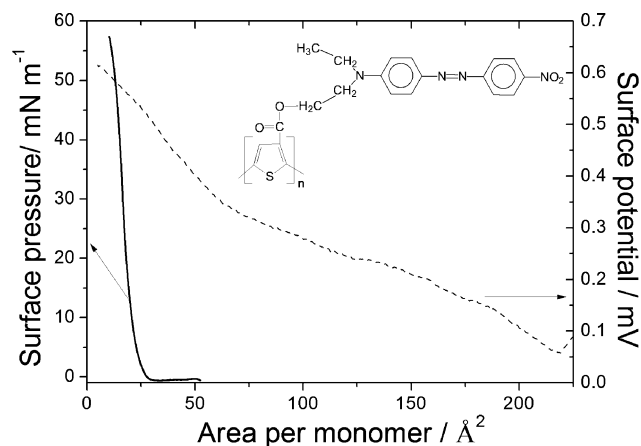
C. A. Olivati  
Depto de Física/IGCE, UNESP,  
CP 178,  
13500-230 Rio Claro, SP, Brazil

photoinduced birefringence of polyazothiophene LB films, aiming at potential optical and electrical applications. In addition, the influence of the film-forming technique employed on these properties was evaluated by comparing results for LB and spin-coated films.

## Materials and methods

The polyazothiophene, referred to here as P3Az (poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane(3-thienyl)ethanoate]), was synthesized through chemical oxidation of an azothiophene monomer. The synthesis of the azomonomer was described earlier [23]. The polymerization was performed as follows: in a nitrogen atmosphere, 2 mmol of azomonomer were dissolved under magnetic stirring in 45 mL of  $\text{CH}_3\text{NO}_2$ . Solid  $\text{FeCl}_3$  (8 mmol) was added quickly to the mixture and the reaction was stirred for 1 h. In the following step, also under nitrogen atmosphere, 180 mL of  $\text{CCl}_4$  were added to the mixture, which was again stirred for 3 h. The product was isolated and purified by precipitation into 1 L of methanol. The presence of unreacted monomer and residual ferric chloride was discarded by testing with thin layer chromatography and spot test with potassium ferricyanide [24], respectively. The polymer was characterized by elemental analyses, nuclear magnetic resonance and Fourier transform infrared (FTIR) spectroscopies, which confirmed the desired structure. The molecular weights of P3Az obtained by high performance size exclusion chromatography in tetrahydrofuran and polystyrene standards were  $M_n=4500$ ,  $M_w=9100$  g/mol. The polymer structure is shown in the inset of Fig. 1.

The polymer was dissolved in chloroform ( $0.22 \text{ mg mL}^{-1}$ ) for Langmuir and LB experiments, while spin-coated films were deposited from chloroform solutions (typical concen-



**Fig. 1** Surface pressure-area ( $\pi$ -A) and surface potential-area ( $\Delta V$ -A) isotherms for pure P3Az on a water subphase.  $T=22$  °C. The inset shows the chemical structure of P3Az

tration  $4 \text{ mg mL}^{-1}$ ) onto different substrates. Spin-coated films were about 30 nm thick as determined by profilometry. LB film thicknesses were estimated from the optical absorption in ultraviolet visible (UV-Vis) spectroscopy measurements. Langmuir and LB films were produced with a KSV5000 Langmuir trough housed in a class 10,000 clean room. Langmuir films were spread onto ultra pure water obtained from a Millipore Milli-Q system (resistivity  $18.2 \text{ M}\Omega \text{ cm}$ ). Film compression was carried out at a barrier speed of  $10 \text{ mm min}^{-1}$ . Surface pressure ( $\pi$ -A) and surface potential ( $\Delta V$ -A) isotherms were obtained with a Wilhelmy plate and a Kelvin probe, respectively, both provided by KSV. LB films were produced by transferring pure P3Az Langmuir films onto hydrophilic glass, SeZn or gold-coated (Au) glass substrates. Spin-coated films were deposited onto the same type of substrate used for LB films fabrication. Y-type LB films with different number of layers (from five to 82 layers) were transferred at a surface pressure of  $35 \text{ mNm}^{-1}$ , with a typical dipping speed of  $2 \text{ mm min}^{-1}$  for the upstrokes and downstrokes. The transfer ratio for the 21 layer-LB films onto glass was approximately 0.8 in the upstrokes and 0.6 in the downstrokes. All experiments were conducted at room temperature ( $22$  °C).

Spin-coated and 21-layer LB films were characterized by FTIR spectroscopy (reflectance and transmission modes) using a Nexus 470 FT-IR,  $4 \text{ cm}^{-1}$  spectral resolution and 64 scans. UV-Vis spectra of the solutions and films (spin-coated and LB) were obtained in a Hitachi U-2001 spectrometer. The emission spectra were measured with a Shimadzu 5301 PC spectrofluorimeter using an excitation slit of 5 and an emission slit of 20 for both films.

For the conductivity measurements, I vs. V curves were obtained at room temperature with a Keithley 238 high voltage source-measure unit. Spin-coated ( $7.6 \text{ mg mL}^{-1}$ ) and 82-layer LB films of P3Az were deposited onto a glass substrate coated with an interdigitated chromium-gold array, whose fabrication is described in detail elsewhere [25]. The conductivity was measured in the dark and upon illumination with a white light of variable power.

The optical birefringence was induced in the films using a polarized  $\text{Ar}^+$  continuous laser at 514 nm, with a polarization angle of  $45^\circ$  with respect to the polarization orientation of the probe beam. The power of the writing laser beam was varied up to 6 mW with a 2.0-mm spot. A low power He-Ne laser at 632.8 nm, passing through crossed polarizers, was used as the probe beam (reading light) to measure the induced birefringence in the samples. Electrochemical measurements were performed with an Autolab PGSTAT 30. The reference electrode was  $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}_{(\text{sat.})}$  (SCE); a  $1.5\text{-cm}^2$  platinum foil was used as auxiliary electrode, and the working electrode was the 21-layer LB film or spin-coated film onto ITO. The

experiments were conducted in HCl 0.05 mol/L solutions at room temperature (22 °C) and sweeping ratio of 50 mV/s. Atomic force microscopy (AFM) images were taken with a microscope from Digital Instruments, Nanoscope IIIA, using the tapping mode.

## Results and discussion

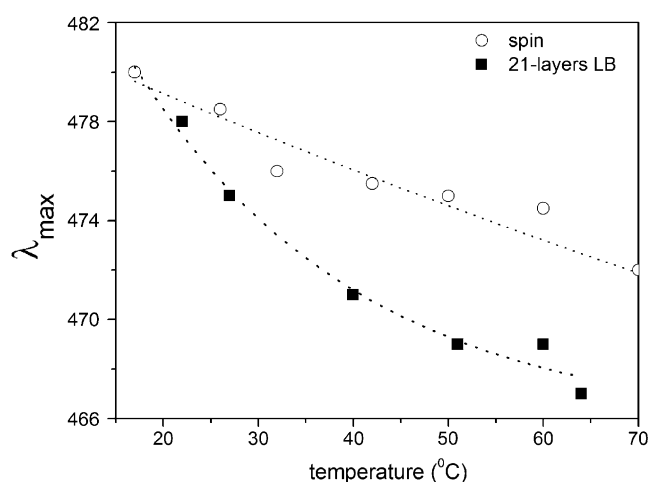
Prior to the fabrication of LB films, the properties of the polymeric film at air–water interface were studied using surface pressure ( $\pi$ ) and surface potential isotherms ( $\Delta V$ ). Figure 1 shows the  $\pi$ -A isotherm for a pure P3Az film, featuring a collapse pressure above approximately 55 mN m<sup>-1</sup> and an extrapolated area of approximately 22–24 Å<sup>2</sup> per monomer for the condensed phase, calculated using the molecular weight of the polymer repeating unit. This extrapolated area is higher than for Langmuir films of poly(3-alkylthiophene) (10–18 Å<sup>2</sup>) [26, 27], being similar to those for methacrylic azopolymers bearing the same azobenzene moiety (22–25 Å<sup>2</sup>) [28, 29]. Therefore, at the air–water interface, poly(3-azothiophene) behaves similarly to azomethacrylic polymers. The surface potential isotherm ( $\Delta V$ -A) indicates formation of non-monomolecular structures (aggregates) in the Langmuir film, as the potential was nonzero for large areas per molecule. The critical area (area where the potential starts to increase) is almost ten times the area per monomer determined by extrapolation of the steep part of the  $\pi$ -A isotherm, instead of two or three times generally observed. Hence, the aggregation that is typical of Langmuir films from polymeric materials [30–32] occurs to a much larger extent in poly(azothiophene). As shown in Fig. 1, the maximum surface potential for condensed monolayers is approximately 0.6 V. Such large surface potential indicates the contribution of large dipole moments in the P3Az molecule, which are perpendicular to the water surface in the condensed phase.

The condensed Langmuir films could be transferred onto several different substrates, including glass, silicon, and gold. For comparison, spin-coated films were also fabricated on these substrates. The film properties were then analyzed with various techniques in an exploration study that is aimed at identifying potential applications in optical electronic devices and sensors. The FTIR spectra of spin-coated and 31-layer LB films of P3Az were recorded in transmission and reflection modes to determine if there was a preferential orientation of the functional groups in the polymer (data not shown). In contrast to results for LB films of other polymers [33, 34], the transmission and reflection spectra were identical, being also the same as for the spin-coated film. Therefore, the LB deposition did not induce a preferential alignment of the functional groups. This analysis also revealed that no chemical modification, e.g., degradation,

occurred in P3Az during the LB deposition. The main features of the FTIR spectra of P3Az, in both films, appear at 3,105 cm<sup>-1</sup> (=C–H stretching of thiophene or aromatic rings), 2,954, 2,953, 2,853 cm<sup>-1</sup> (CH<sub>2</sub>; CH<sub>3</sub> stretching), 1,735 cm<sup>-1</sup> (C=O ester stretching), 1,516 cm<sup>-1</sup> (aromatic—N=O) and 1,337 cm<sup>-1</sup> (N=O stretching).

The UV-Vis and photoluminescence spectra of LB and spin-coated films were recorded at room temperature. The absorbance spectra display a peak at 470 nm for both films. The absorbance of LB films increases linearly with the number of layers, pointing to a homogeneous deposition procedure. Identical UV-Vis spectra were obtained for s- and p-polarized light in LB films of various numbers of layers, thus, confirming the conclusion from FTIR data that there is no preferential alignment of the polymer chains [22]. Polythiophenes are luminescent, but incorporation of azobenzene moieties in the side chain could hamper the photoluminescence (PL). This was not the case, though, for both 31-layer LB and spin-coated film-exhibited PL maxima at 640 nm. In short, the deposition method did not affect the film emission or absorption properties at room temperature.

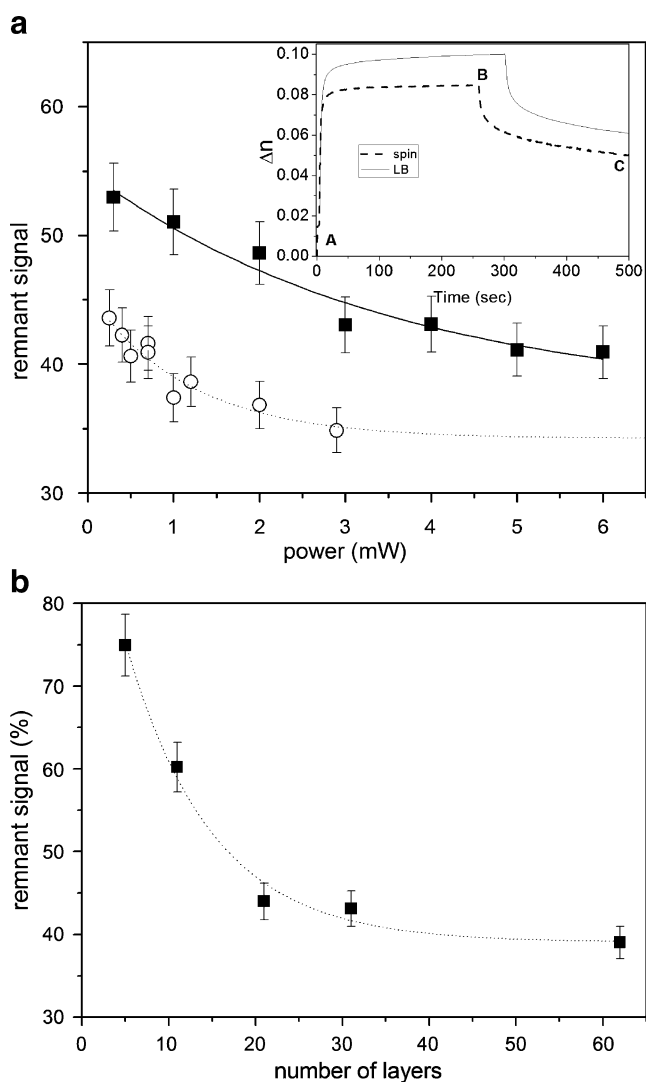
Thermochromic effects were observed in spin-coated and 31-layer LB films when the UV-Vis spectra were collected at different temperatures, in the range between 10 and 70 °C. The absorbance at 480 nm ( $\lambda_{\text{max}}$  at 10 °C) decreased only slightly (around 0.01) upon heating the films, but  $\lambda_{\text{max}}$  shifted significantly to lower values upon heating, as shown in Fig. 2. Such thermochromic effects in polythiophenes are generally associated with the transition from a planar to a nonplanar structure of the polymer main chains, which leads to a decrease in the conjugation length and in  $\lambda_{\text{max}}$  [23]. The decrease was more accentuated in the LB films, probably because the molecular packing induced by the LB method facilitates the transition to a nonplanar



**Fig. 2** Wavelength of maximum absorption ( $\lambda_{\text{max}}$ ) at different temperatures for spin-coated and LB films. The lines are only to guide the eyes

structure. For both films, the initial spectrum is obtained when the temperature decreased from 70 to 10 °C, showing that the process is reversible.

The photoinduced birefringence in spin-coated and LB films, i.e., their optical storage capability, was studied using several laser powers. We analyzed the maximum transmitted signal, which is related to the photoinduced birefringence, with laser powers from 0.3 to 8 mW in an interval of 300 s. In all cases, signal saturation was reached in no more than 150 s. The maximum transmitted signal increased with the laser power up to 1 mW, after which saturation was reached. The inset of Fig. 3a shows the optical storage curves obtained with 3 mW for both films. The photoinduced birefringence ( $\Delta n$ ) was calculated from the transmitted signal according to:  $\Delta n = \frac{\lambda}{\pi d} \sin^{-1} \sqrt{\frac{I}{I_0}}$ ,

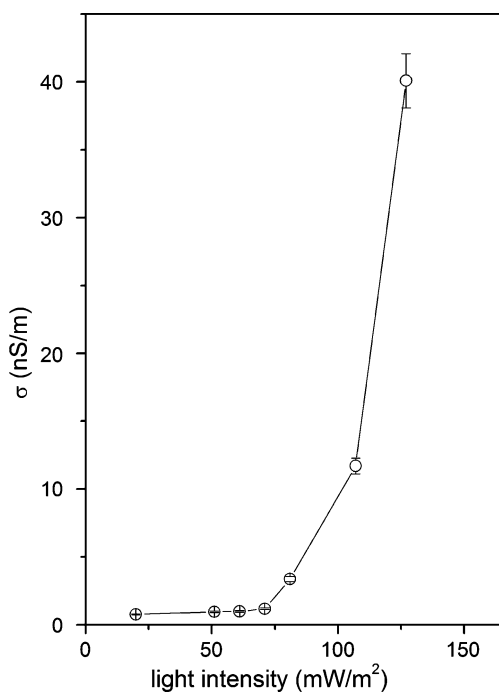


**Fig. 3** **a** Effect of the laser power on remnant signal for (filled square) LB and (empty circle) spin-coated films. **b** Remnant signal for LB films with different numbers of layers obtained with a pump laser power of 4 mW. The inset of **a** shows the optical storage curve for P3Az spin-coated and LB films. The lines are only to guide the eyes

where  $\lambda$  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. The optical storage features were similar to other azopolymers [3, 4, 29]. Due to the random orientation of chromophores, no transmission of the probe beam passing through the second polarizer was observed until the writing beam was switched on (time A). The *trans*–*cis*–*trans* isomerization cycles for the azobenzene chromophores then took place, inducing reorientation of chromophores. Those with dipole moment perpendicular to the light polarization no longer absorb, remaining in that orientation. After several photoisomerization cycles, a large number of chromophores will be aligned perpendicularly to the light polarization, thus, leading to birefringence in the sample. After the writing beam was switched off (time B), chromophore relaxation occurred. Nevertheless, a considerable number of molecules remained oriented, which gave rise to a remnant birefringence (time C). Higher values of remnant birefringence indicate that more information can be stored in the film. The information can be erased thermally or by using circularly polarized laser.

The calculated values of maximum birefringence for spin-coated and 31-layer LB films were 0.11 and 0.13, respectively. Similar results were obtained for LB films with different numbers of layers and are consistent with data for films of methacrylic azopolymers [35]. The time to achieve 50% of the maximum birefringence ( $T_{50\%}$ ) decreased with the laser power up to 3 mW, in a sharper way for the LB film, to reach a minimum time of 3 s. The writing times are of the same order of magnitude as for LB films of other azopolymers [29]. The remnant signals which measured 200 s after the laser was turned off also decreased with the laser power for both films (Fig. 3a). However, the values for the LB film are almost 10% higher than for the spin-coated film, probably due to differences in the molecular packing (LB films tend to be denser) [34]. Experiments with LB films containing five, 11, 21, 31, and 62 layers showed a decreasing remnant birefringence with increasing number of layers, as seen in Fig. 3b (4 mW excitation laser power). The remnant values decreased up to 20 layers or so, then tended to the value of the spin-coated film. This behavior is associated with the decrease in ordering in the LB film upon the deposition of a larger number of layers [3].

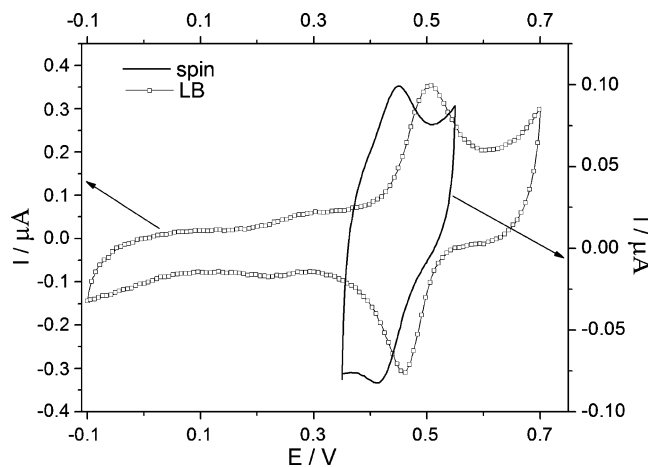
The conductivity measurements were performed on an interdigitated chromium–gold array for the P3Az spin-coated film. Attempts to deposit P3Az on the gold-array electrode with the LB technique resulted in poor covering of the electrode, even after depositing several layers. Therefore, electrical measurements were not performed in LB films. From the linear fit of  $I$  vs.  $V$  curves (not shown), it is possible to estimate the conductivity ( $\sigma$ ) of the material, using the parameters  $l$  (film thickness=100 nm)



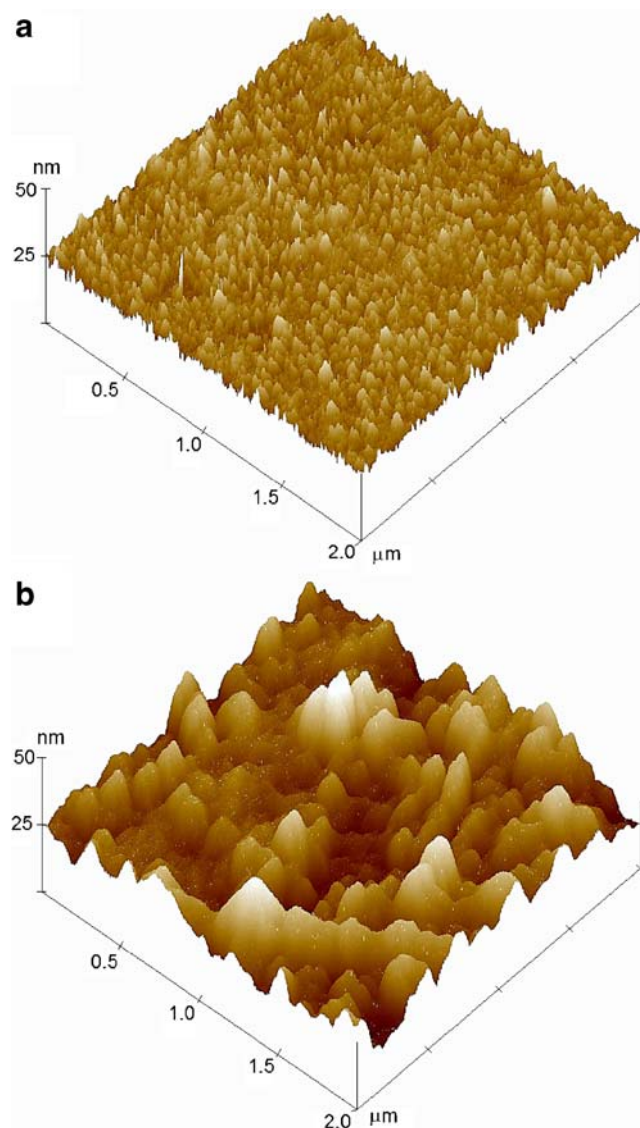
**Fig. 4** Conductivity ( $\sigma$ ) versus light intensity for P3Az spin-coated film

and  $A$  (area =  $2 \mu\text{m}^2$ ). The conductivity measured in the dark was  $8 \times 10^{-10}$  S/m, which is in agreement with the literature for neutral regio-random polythiophenes [14, 36, 37]. Under illumination, the conductivity was practically constant up to  $75 \text{ mW/cm}^2$ , and then increased to  $4 \times 10^{-8}$  S/m at  $125 \text{ mW/cm}^2$ , as shown in Fig. 4. Such increase in conductivity revealed the photoconductive nature of the material, with photoconductivity being defined by an increased conductivity caused by irradiation [38]. The simplest process of photoconduction occurs when a photon is absorbed and an electron is promoted from the highest occupied molecular orbital to the lowest unoccupied molecular orbital [39]. This process generates an electron-hole pair, which increases the conductivity of organic semiconductors and some polymers, including the conjugated ones. In the present case, the effect is probably related only to the conjugated thiophene backbone, thus, showing that the azobenzene moiety in the side chain does not affect the photoconductivity of the polythiophene chain.

The electroactivity of spin-coated and LB films of P3Az were investigated by cyclic voltammetry. The polymer is soluble in acetonitrile and in other organic solvents commonly used in electrochemical characterization; therefore, the electroactivity measurements were performed in aqueous acid media. Figure 5 shows the cyclic voltammograms for spin-coated and LB films deposited onto ITO, using a sweeping rate of  $50 \text{ mV s}^{-1}$  in electrolytic solutions of  $0.05 \text{ mol L}^{-1}$  HCl. The range of the potential is different for spin-coated and LB films because the cyclic voltammo-



**Fig. 5** Cyclic voltammograms for spin-coated and LB films from P3Az with a sweeping rate of  $50 \text{ mV s}^{-1}$ . All measurements were carried with  $0.05 \text{ mol L}^{-1}$  HCl



**Fig. 6** AFM images of the **a** spin-coated film; **b** 21-layer LB film

grams depend on the type of film [40, 41]. A redox pair appears in both films. In copolymers of azothiophenes with alkylthiophenes, two features are common in cyclic voltammograms recorded in acetonitrile: (1) the electrochemical oxidative doping and reductive dedoping of polyconjugated system and (2) the oxidation or reduction of the chromophoric side chain [6, 10]. For the homopolymer of polyazothiophene (our case), only one redox pair was observed. For spin-coated films, a redox pair appears approximately 0.45 V (oxidation) and 0.42 V (reduction). Attempts to use more concentrated acid solution led these peaks to disappear, and the polymer was no longer electroactive in spin-coated film (results not shown). In a control experiment with spin-coated films of poly(3-octylthiophene), in HCl, one redox pair could be observed at approximately 0.3 V. Thus, the redox pair may be attributed to the conjugated chain, although the influence from the azo side chain cannot be completely ruled out. Experiments with copolymers with different proportions of octylthiophene and 3-AzT are being carried out to further explore the electrochemical behavior in HCl. For the LB films, the redox pair was observed at 0.50 V (oxidation) and 0.45 V (reduction) in Fig. 5. In contrast to the spin-coated ones, the LB film remained electroactive even in a more concentrated HCl solution, though with a lower electroactivity probably due to film degradation. The differences in the voltammograms for spin-coated and LB films may be attributed to distinct film morphologies, which can be denser in LB films [40].

In fact, the AFM images shown in Fig. 6 illustrate the differences in film morphology. While the spin-coated film had a lower roughness (rms=1.3 nm), with small, randomly distributed aggregates, the LB film displayed globular structures with a larger roughness of 5.2 nm (rms). The azopolymer was, therefore, aggregated to a larger extent in the LB films. The differences in surface roughness can lead to distinct wettabilities and, hence, affect the electrochemical response.

## Conclusions

P3Az films were successfully obtained with the LB technique whose properties were investigated and compared with those from spin-coated films. The P3Az films were shown to possess interesting properties, such as photoluminescence, photoconductivity, thermochromism, electroactivity, and photoinduced birefringence, and the latter three properties were enhanced with the use of LB deposition. This slightly superior performance of LB films, in comparison to spin-coated films, is probably due to the differences in molecular packing and film surface morphology. Most significantly, the observation of a rich variety of properties indicates that P3Az is promising for further

studies envisaging applications in optical storage, surface relief gratings, thermal, optical, and electrochemical sensors, in addition to other devices.

**Acknowledgments** The financial support from FAPESP, CNPq, and IMMP–MCT (Brazil) is gratefully acknowledged.

## References

- Natansohn A, Rochon P (2002) *Chem Rev* 102:4139
- Viswanathan NK, Balasubramanian S, Li L, Kumar J, Tripathy SK (1998) *J Phys Chem B* 102:6064
- Mendonça CR, Dhanabalan A, Balogh DT, Misoguti L, dos Santos DS Jr, Pereira-da-Silva MA, Giacometti JA, Zilio SC, Oliveira ON Jr (1999) *Macromolecules* 32:1493
- Oliveira ON Jr, dos Santos DS Jr, Balogh DT, Zucolotto V, Mendonça CR (2005) *Adv Colloid Interface Sci* 116:179
- Ribeiro PA, Balogh DT, Fonseca JLC, Giacometti JA (2004) *Macromolecules* 37:2618
- Zargorska M, Kulszewicz-Bajer I, Pron A, Raimond P, Kajzar F, Attias AJ (1999) *Synt Met* 102:1141
- Della-Casa C, Fraleoni-Morgera A, Costa-Bizzarri P, Lanzi M (2001) *Synt Met* 124:467
- Chittibabu KG, Li L, Kamath M, Kumar J, Tripathy SK (1994) *Chem Mater* 6:475
- Mochizuki H, Nabeshima Y, Kitsunai T, Kanazawa A (1999) *J Mater Chem* 9:2215
- Zargorska M, Kulszewicz-Bajer I, Pron A, Raimond P, Kajzar F, Attias AJ (1998) *Macromolecules* 31:9146
- Pizzoferrato R, Sarcinelli F, Angeloni M (2001) *Chem Phys Lett* 343:205
- Fraleoni-Morgera A, Della-Casa C, Lanzi M, Costa-Bizzarri P (2003) *Macromolecules* 36:8617
- Fraleoni-Morgera A, Della-Casa C, Costa-Bizzarri P, Lanzi M, Missiroli A (2005) *Macromolecules* 38:3170
- Della-Casa C, Costa-Bizzarri P, Lanzi M (2001) *Synth Met* 138:409
- Aubertin F, Zhao Y (2004) *J Polym Sci A Polym Chem* 42:3445
- Lanzi M, Paganin L, Costa-Bizzarri P (2004) *Eur Polym J* 40:2117
- Levesque I, Leclerc M (1997) *Macromolecules* 30:4347
- Gan LH, Xia X, Cham CY, Hu X, Zhao X (2003) *Polym Adv Techn* 14:260
- Oliveira ON Jr, He JA, Zucolotto V, Balasubramanian S, Li L, Nalwa HS, Kumar J, Tripathy SK (2002) *Handbook of polyelectrolytes and their applications*. American Scientific, New York
- Petty MC (1996) *Langmuir–Blodgett films: an introduction*. Cambridge University Press, Cambridge
- Santos DS Jr, Bassi A, Misoguti L, Ginani MF, Oliveira ON Jr, Mendonça CR (2002) *Macromol Rapid Commun* 23:975
- Olivati CA, Ferreira M, Cazati T, Balogh DT, Guimarães FEG, Oliveira ON Jr, Faria RM (2003) *Chem Phys Lett* 381:404
- Gonçalves VC, Balogh DT (2006) *Eur Polym J* 42:3003
- Feigl F, Anger V (1972) *Spot tests in inorganic analysis*. Elsevier, Amsterdam
- Olivati CA, Bianchi RF, Marconi FM, Balogh DT, Faria RM (2002) *Mol Cryst Liq Cryst* 374:451
- Xu G, Bao Z, Groves JT (2000) *Langmuir* 16:1834
- Somanathan N, Dhathathreyan A, Wegner G (1999) *Current Science* 76:1566
- Dhanabalan A, Balogh DT, Riul A Jr, Giacometti JA, Oliveira ON Jr (1998) *Thin Solid Films* 323:257

29. Dhanabalan A, Mendonça CR, Balogh DT, Misoguti L, Constantino CJL, Giacometti JA, Zilio SC, Oliveira ON Jr (1999) *Macromolecules* 32:5277
30. Dhanabalan A, Riul A Jr, Oliveira ON Jr (1998) *Supramol Sci* 5:75
31. Constantino CJL, Dhanabalan A, Riul A Jr, Oliveira ON Jr (1999) *Synth Met* 101:688
32. Dhanabalan A, Malmonge JA, Riul A Jr, Faria RM, Oliveira ON Jr (1998) *Thin Solid Films* 808:327
33. Pasquini D, Balogh DT, Antunes PA, Constantino CJL, Curvelo AAS, Aroca RF, Oliveira ON Jr (2002) *Langmuir* 18:6593
34. Ferreira M, Constantino CJL, Olivati CA, Vega ML, Balogh DT, Aroca RF, Faria RM, Oliveira ON Jr (2003) *Langmuir* 19:8835
35. Mendonça CR, Santos DS Jr, Balogh DT, Dhanabalan A, Giacometti JA, Zilio SC, Oliveira ON Jr (2001) *Polymer* 42:6539
36. Li L, Chittibabu KG, Chen Z, Chen JI, Marturunkakul S, Kumar J, Tripathy SK (1996) *Optics Comm* 125:257
37. Chen TA, Wu X, Rieke RD (1995) *J Am Chem Soc* 117:233
38. Greenham NC, Friend RH (1995) *Solid State Physics* 49:1
39. Barth S, Bassler H, Wehrmeister T, Mülllen K (1997) *J Chem Phys* 106:321
40. Ferreira M, Wohnrath K, Oliveira ON Jr (2003) *Synth Met* 135:455
41. Wohnrath K, Garcia JR, Nart FC, Batista AA, Oliveira ON Jr (2002) *Thin Solid Films* 402:272