

Langmuir–Blodgett and Langmuir–Schaefer films of poly(5-amino-1-naphthol) conjugated polymer

C.P.L. Rubinger^a, R.L. Moreira^{a,*}, L.A. Cury^a, G.N. Fontes^a,
B.R.A. Neves^a, A. Meneguzzi^b, C.A. Ferreira^b

^aDepartamento de Física, ICEx, Universidade Federal de Minas Gerais, C.P. 702, 30123-970 Belo Horizonte, MG, Brazil

^bDepartamento de Materiais, Universidade Federal do Rio Grande do Sul, 90035-190 Porto Alegre, RS, Brazil

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Abstract

Langmuir-type films of poly(5-amino-1-naphthol) conductive polymer were formed at the air/water interface. The surface pressure versus molecular area isotherms of the polymeric layers showed a high tendency to aggregate and non-monomolecular behavior on the water surface. Langmuir–Blodgett (LB) and Langmuir–Schaefer (LS) procedures have been successfully used to transfer the Langmuir films of this polymer onto hydrophilic silicon substrates. Atomic force microscopy images showed that the films obtained by the LS method have much better quality than those obtained by the LB one. In particular, we have obtained uniform and smooth LS films covering practically all the substrate, while the LB films showed rather aggregated material, only partially covering the substrate.

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1. Introduction

Poly(5-amino-1-naphthol), henceforth PAN, is a conductive organic polymer, which is usually synthesized on glassy carbon or platinum electrodes by electro-polymerization of 5-amino-1-naphthol [1–5]. Since this monomer contains two functional groups, –OH and –NH₂, which can both be electrochemically oxidized, the pH of the media plays a key role in the polymer's formation. Indeed, PAN is obtained in either organic or aqueous acidic media, the polymerization occurring via the oxidation of the amine group. On the other hand, by using high pH media, the polymerization occurs via the hydroxyl group, leading to the formation of poly(naphthalene oxide). In the first case, the obtained polymer is quite adequate for protection of metallic surfaces against corrosion. This is due to the similarity between its structure and that of polyaniline, which is well known for its good passivating properties with respect to iron [6,7]. Moreover, the free reactive –OH groups allow further surface

reactions, thus conferring excellent properties to the PAN film as a primer coating, with good compatibility with other polymeric materials [2,4]. PAN films can also be employed as the active element of molecular electronic devices, owing to their semiconductive properties [8]. In view of the applications cited above, the polymeric films must satisfy specific requirements concerning their uniformity, roughness, thickness, etc., which can be achieved by using Langmuir methods.

Langmuir–Blodgett (LB) technique is recognized as a useful tool to prepare thin molecular films, ranging from one to several tens of molecular layers. In general, it is applied to amphiphilic molecules, i.e., to systems that possess distinct polar (hydrophilic) and non-polar (hydrophobic) parts, which can form stable Langmuir films at the air/water interface, being subsequently transferred onto chosen substrates [9]. In recent years, the usefulness of this technique has been progressively extended to non-amphiphilic macromolecules such as polymers [10–12], biomolecules [13] and fullerenes [14]. Nevertheless, although relatively stable films of these materials could be formed at the air/liquid interface, the transferred films are not necessarily monomolecular, because of the rigidity of the molecules and to other intermolecular interactions [12,15].

* Corresponding author. Tel.: 55 31 3499 5624; fax: 55 31 3499 5600.

E-mail address: bmoreira@fisica.ufmg.br (R.L. Moreira).

However, the terms Langmuir film and Langmuir monolayer are employed to designate stable organic films at the air/liquid interface, whether they were monomolecular or not (they can form clusters or aggregates, for instance) [12,15–20].

Recently, there has been an increasing interest in the use of Langmuir methods in molecular electronics, because of the possibility to build up organic materials and devices with controlled structure and architecture. In particular, some success has been achieved with ultrathin film deposition of polythiophenes and polyanilines [21–24]. In a previous work, we investigated the polymer/substrate adhesion forces of LB-type PAN films transferred on silicon substrates [25]. In the present paper, we report on the preparation and characterization of Langmuir and LB-type PAN films. The thermodynamics and stability of the Langmuir films at the air/water interface are investigated at different subphase conditions and compression rates. Both vertical (LB) and horizontal (Langmuir–Schaefer, LS) lifting procedures allowed the transfer of the Langmuir films to a solid substrate, under optimized transfer ratios. Atomic force microscopy (AFM) was used to characterize the resulting LB- and LS-PAN films.

2. Experimental

2.1. Synthesis

PAN films were obtained electrochemically on platinum electrodes in acidic aqueous solutions (1 M of HClO_4 , from Merck) containing 10^{-3} M of the monomer (commercial 5-amino-1-naphthol, from Aldrich). Electrochemical polymerization was performed by potential cycling for 15 min at a sweep rate of $\pm 50 \text{ mV s}^{-1}$, between 0 and +0.75 V. The schematic structure of the polymer obtained (PAN) is shown in Fig. 1. Note the similarity between the PAN structure and the emeraldine form of polyaniline, which simply does not contain the hydroxyl groups [6].

2.2. Langmuir and LB-type films

Distilled water purified in a Millipore Milli-Q system was used as the subphase (electrical resistivity = $18.2 \text{ M}\Omega \text{ cm}^{-1}$ and pH 5.6 at 20°C). The spreading solution was obtained by dissolving the polymer in dimethylacetamide (DMAc) to a final concentration of 0.20 mg/ml. Freshly prepared solutions (400 μl) were carefully spread onto the water subphase, in a Teflon[®] trough. After complete evaporation of the solvent (15 min), the PAN molecules were symmetrically compressed

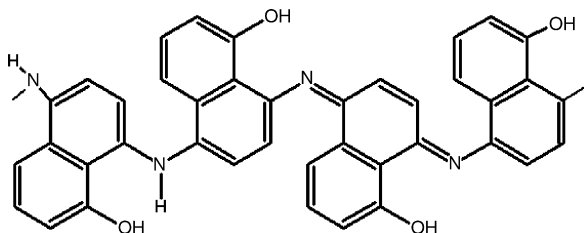


Fig. 1. A schematic representation of the poly(5-amino-1-naphthol) structure.

by two hydrophilic barriers (Delrin[®]). Surface pressure versus molecular area isotherms (based upon the Wilhelmy method) and LB depositions were carried out in a KSV Minitrough2 instrument (325 mm \times 75 mm). The PAN layers were compressed at several rates ranging from 2 to 50 mm/min. The subphase temperature was controlled within $\pm 0.5^\circ\text{C}$ by a closed-cycle Nova Ética thermal bath connected to the LB trough. Adding diluted HCl or NaOH solutions enabled us to control the subphase pH. The mean molecular area values were calculated based on the molecular weight of the monomeric repeat unit (159 g/mol). Cleaned hydrophilic silicon wafers were used as substrates. LB films were transferred onto the silicon substrates at several dipping speeds. The best results were achieved for depositions made at very low dipping speeds ($< 1 \text{ mm/min}$), with fixed constant surface pressure (18 mN/m) and temperature (22°C). Langmuir–Schaefer (LS) films [26] were transferred using the same experimental conditions, by clasping horizontally the compressed Langmuir film and lifting the substrate upwards very slowly (0.5 mm/min). A scheme of the experimental setup used for LB and for LS transfers onto Si substrates is presented in Fig. 2.

2.3. Morphological characterization

AFM experiments were performed with a Nanoscope IV Multimode (Veeco Instruments) on intermittent contact mode using conventional silicon cantilevers. In such mode, the cantilever that holds the tip is forced to oscillate near its resonance frequency and the tip taps the sample surface at a typical rate of 200 up to 500 times per scanning point, enabling high lateral resolution. It is important to stress that this rate depends on the actual vibrating frequency of the cantilever, scan speed and the number of pixels per scan line. In the present work, a cantilever with a resonant frequency of 284.9 kHz and a spring constant of 53 N/m was employed [27]. Also, the shear forces acting upon the sample surface are greatly diminished when compared with conventional AFM contact mode of operation. Phase contrast images were also acquired simultaneously with topography images by monitoring, with a lock-in, the phase lag between the oscillation driver and the actual response of the cantilever. Although phase images are not very sensitive to height differences, they are very sensitive to topographic features like borders and also to compositional differences [28]. In the present experiments, Si substrates were

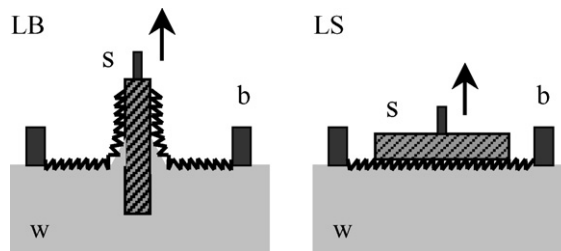


Fig. 2. Scheme of Langmuir–Blodgett (left) and Langmuir–Schaefer (right) experimental setups, showing the water subphase (w), the delrin[®] barriers (b) compressing the polymeric film in the air/water interface, and the Si substrates during the transfers (s).

preferred because of their low rms (root mean square) roughness prior to deposition, measured as $(1.3 \pm 0.2) \text{ \AA}$, after several runs.

3. Results and discussion

The surface pressure (π) versus molecular area (A) isotherms of a floating layer (Langmuir film) provide information about the thermodynamic properties of molecules at the air/water interface. Hysteresis and cycling measurements provide additional information about the film stability. Together, these characteristics constitute powerful tools for fabricating and studying organized, molecular thin solid films [9,16,26,29].

In order to obtain Langmuir PAN films on the water surface, we have first optimized several parameters, such as the solvent used to spread the polymer, the polymer concentration and the subphase pH. DMAc and *n*-methylpyrrolidone (NMP) gave better results as spreading solvents than DMAc/chloroform mixtures. The latter solvent mixture tends to produce highly agglomerated polymer regions, which are visible on the water surface. The results with NMP were similar to those with DMAc. However, we preferred to use DMAc due to its lower toxicity. The optimum PAN/DMAc concentration (0.20 mg/ml) was determined from empirical tests by establishing the amount of spreading solution (400 μ l). For pH values varying from 3.5 to 10, we observed little or negligible influence on the π - A isotherms. Thus, we decided to maintain the pH of the subphase at its normal value (5.6) for all subsequent experiments. Taking into account these fixed parameters, Fig. 3 shows the π - A isotherms recorded for virgin PAN films at 22 °C, for different compression speeds: 2, 10 and 50 mm/min. The three curves show a monotonic increase in the surface pressure with decreasing surface area. Extrapolation of the isotherms to zero pressure leads to a very low mean molecular area (MMA) of approximately 5 \AA^2 , per repeat unit. These isotherms exhibit the typical shape for condensed macromolecular Langmuir films [9,16]. The slopes of the three isotherms are very close, indicating similar compressibility moduli for a large pressure

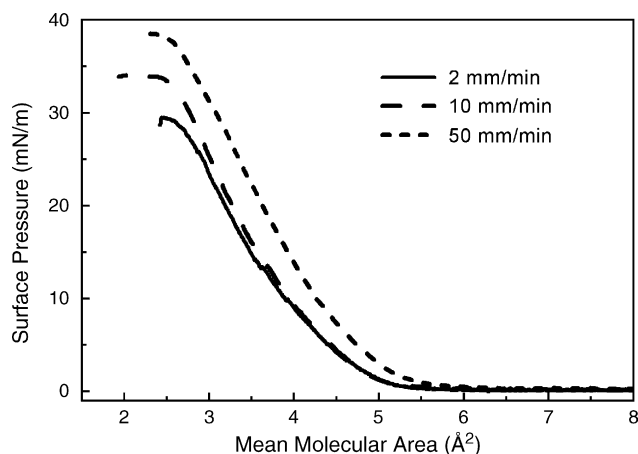


Fig. 3. Surface pressure versus molecular area (π - A) isotherms of PAN films at the air-water interface, for different symmetrical compression speeds (2, 10 and 50 mm/min). The water subphase temperature was 22 °C. The area is given for the polymer repeat unit (monomer).

interval (at least between 15 and 25 mN/m). The effect of compression speed is more prominent for complex molecules than for simple ones. Our results show that the isotherms of the PAN molecular film are slightly shifted to smaller areas for lower compression speeds, which agrees with the usual behavior observed for other polymers (lower speeds allow better molecular packing) [11,15,20,26,29,30]. Moreover, the collapse pressure also decreases for lower compression speeds. This behavior is also expected and can be attributed to the higher rigidity of the polymer layers when compared to simple amphiphilic molecules [30,31]. The results of Fig. 3 allow us to choose a compression speed of 10 mm/min (approximately $0.50 \text{ \AA}^2/\text{min}$) as an adequate compression rate, which is low enough to permit chain rearrangement, but relatively high to give smooth Langmuir isotherms and a high collapse pressure.

The molecular area occupied by the Langmuir film, approximately 5 \AA^2 , is much lower than what we can predict theoretically for the PAN molecule (22 \AA^2). Nevertheless, the monotonic isotherms of Fig. 3 indicate the formation of Langmuir-type films, irrespective of the compression speed. We have also used different subphase temperatures, but the best π - A isotherms were obtained at room temperature, because at higher temperatures we have lower collapse pressures, while for lower temperatures we have higher polymeric chain rigidity, as also observed for other macromolecular systems with the tendency to form aggregates [32–34].

In order to investigate the stability of the Langmuir PAN films, we performed successive compression-decompression cycles at the optimized conditions (pH 5.6, compression-decompression speeds of 10 mm/min) at 22 °C, attaining a maximum pressure of 20 mN/m, well below the collapse point (above 30 mN/m, at this temperature). The results are presented in Fig. 4. The polymeric film does not show complete reversibility, in the sense that the MMA decreases in subsequent cycles, showing an irreversible behavior that can be related to some instability of the molecular layer. The origin of the hysteresis observed in this figure for the Langmuir PAN film is associated with the manifestation of strong intermolecular interactions during compression of the monolayer. This is a common feature in any deformable system, since the area inside

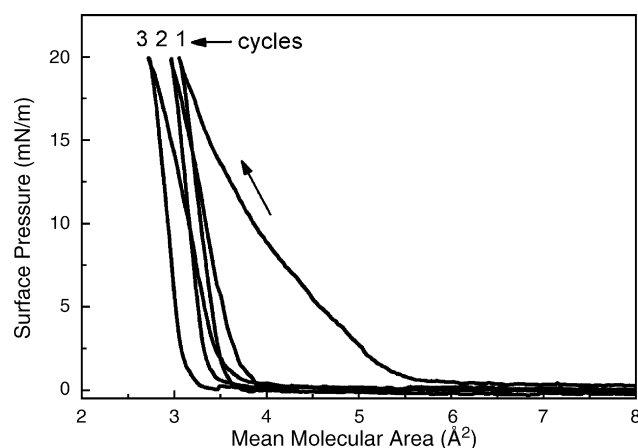


Fig. 4. π - A compression-decompression cycles of a Langmuir PAN film at the air-water interface, at 22 °C and 10 mm/min rates.

the curve is proportional to the energy spent in producing a new molecular arrangement [16]. On the other hand, the reduction of the MMA by the compression cycle indicates some packing rearrangements and/or aggregate formation during the compression runs, similarly to what is observed in lignins [17] and other materials showing complex molecular shapes [11], although a partial dissolution of the Langmuir PAN films in the water subphase can also occur.

We now present the results obtained for the LB transferred PAN films. By using the vertical dipping method, schematized in Fig. 2, we found that Z-transferred films with transfer ratios (TR) close to 1 could be obtained only for the first upward stroke of hydrophilic Si substrates, at 18 mN/m and 22 °C (in virgin samples compressed at 10 mm/min, pH 5.6, dipping speed of 0.5 mm/min). Using lower pressures leads to TR lower than 1. It is significant to point out that the optimized pressures for LB deposition of several polyaniline derivatives range from 18 to 25 mN/m [35,36], with a fair resemblance to our system's behavior. All attempts to make multiple depositions without any molecular aids (e.g., surfactants, salts, acids) failed. In this sense, we remark that the behavior of the Langmuir and LB films of our material is somewhat similar to fatty alcohols and other aromatic compounds containing hydroxyl groups: their Langmuir films are very stable, their isotherms have no or negligible dependence on the subphase pH (in the interval 2–10), and yet multiple LB films cannot be formed [9]. Thus, we only investigate the morphology of (pure) single-layer LB-PAN films. Fig. 5a presents an AFM image of a LB-PAN film obtained by the vertical lifting method onto Si substrate. The dark gray regions indicate the Si substrate, as evidenced by phase contrast images (not shown in this figure), whereas the gray and light gray regions indicate PAN covered regions. As it can be seen, the substrate was only partially covered, despite the TR = 1. Analysis of AFM images of larger areas permits the determination of surface coverage (40%), height and roughness. The vertical LB-PAN films show the presence of flat disordered agglomerates with varying height, mostly on the order of 50 Å, very similar to that reported for thin LB films of polyaniline [35]. The surface roughness (rms) shown by the LB-PAN sample was relatively high, attaining 25 Å.

Low surface coverage often occurs in LB-films of non-amphiphilic molecules, even for TR = 1. In the case of low molecular weight compounds, this phenomenon is attributed to molecular rearrangement during or after deposition, leading to the formation of bilayers or clusters, due to hydrogen bonds between the molecules [19,37–39]. On the other hand, in the case of high molecular weight compounds, such as polymers, the reason would be the desorption of the material followed by its partial dissolution in the subphase, owing to the complex forces acting at the triple line for these rigid materials, during the Langmuir–Blodgett transfer [9,16].

Due to the high rigidity of the polymeric film, we used the horizontal lifting (or Langmuir–Schaefer) method to transfer the Langmuir PAN films (maintaining the other parameters used in the vertical deposition). In this case, the substrate does not directly touch the subphase (semi-dry process) [40], so that the floating monolayer is subject to less disruptive forces than in

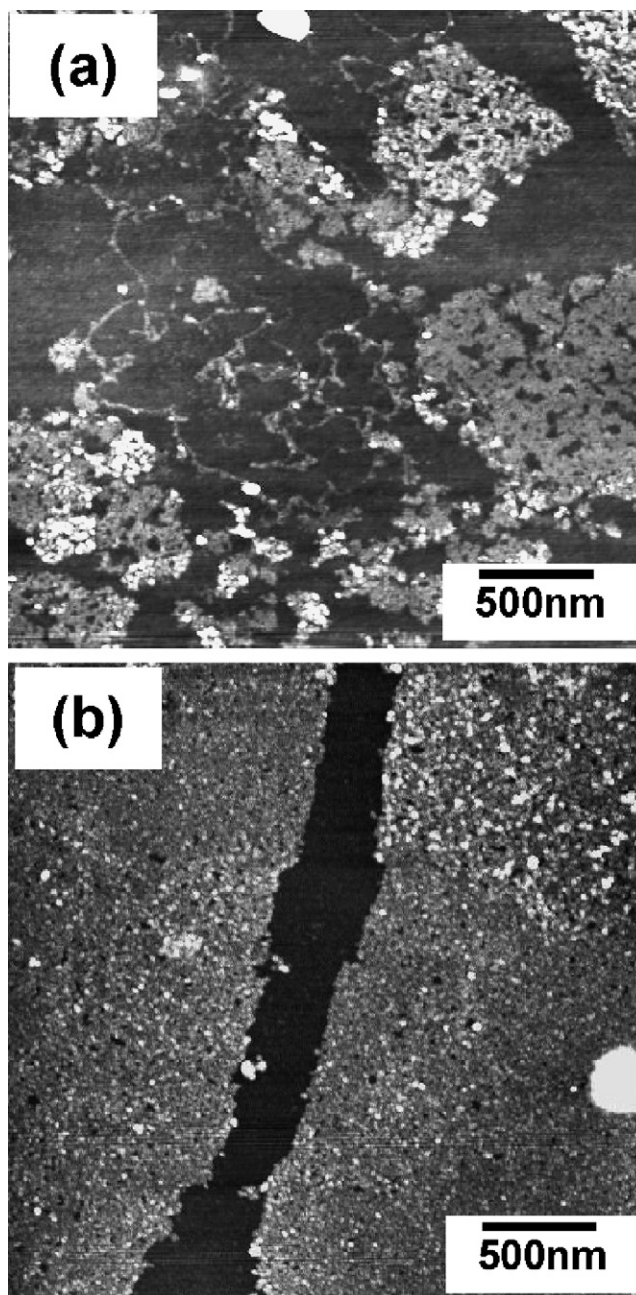


Fig. 5. (a) AFM topographic image of a LB-PAN film on Si substrate. The film was transferred during the first upward stroke at an established pressure of 18 mN/m, for a subphase temperature of 22 °C, after compression at 10 mm/min. (b) AFM topographic image of a LS-PAN film on Si substrate, obtained under the same experimental conditions as in (a). The scales of the figures are 3 μm \times 3 μm .

the case of LB method, as can be inferred from Fig. 2. Fig. 5b shows an AFM image of a horizontally transferred LS-PAN single-layer. We used this particular image because in this sample region there is a crack in the film (dark gray region) that allows us to measure the height of the covering film (gray region) and also because, by using the phase contrast technique, we could differentiate the polymer from the silicon substrate (the dark gray region in Fig. 5b presents roughness and viscoelastic values coherent with those of Si). In general, AFM

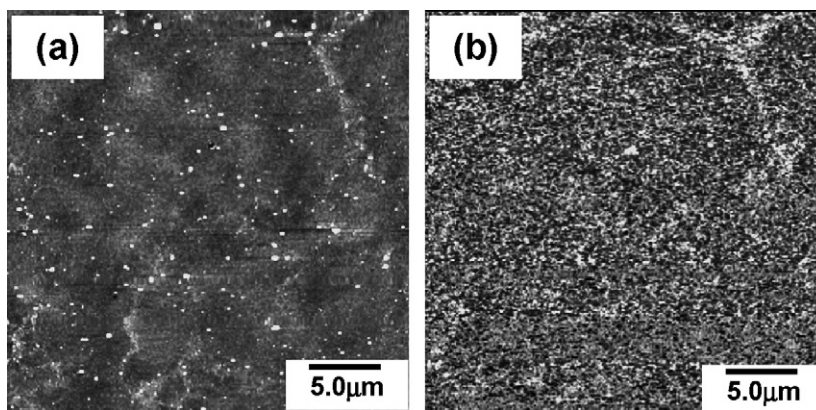


Fig. 6. AFM topographic (a) and phase contrast (b) images of a LS-PAN film on Si substrate, showing a smooth uniform polymeric film. The scales of the figures are $25 \mu\text{m} \times 25 \mu\text{m}$.

images of the LS-PAN films show flat (surface roughness $\sim 10 \text{ \AA}$) and relatively homogeneous films, with mean heights of about 50 \AA , over more than 80% of the sample surface. These results are confirmed by measuring different regions of several LS-PAN samples, on several scales. For example, Fig. 6 presents the topographic (a) and phase contrast (b) images of a LS-PAN single-layer film with a $25 \mu\text{m} \times 25 \mu\text{m}$ scale. Note that this film is very uniform (and homogeneous) and that the substrate is completely covered by the polymer. We also observed that the film is relatively smooth (average height and rms roughness as above), but we did not discern any in-plane chain orientation.

Having shown that Langmuir films of PAN can be formed on the water surface and transferred to a Si substrate, let us now discuss the unexpected measured values for the MMA of the Langmuir films and heights of the solid films. While the predicted values from the molecular structure (Fig. 1) were, respectively, $(22 \pm 2) \text{ \AA}^2$ for the MMA and $(9 \pm 1) \text{ \AA}$ for the film height, the experimental results were approximately 5 \AA^2 (Langmuir isotherms) and 50 \AA (AFM). We note first that there is a good mass conservation, which confirms our proposition that the Langmuir PAN films were formed by aggregated polymeric chains. A significant finding is that polyaniline, a material very similar to PAN as previously remarked, shows analogous behavior: the observed MMA of their Langmuir films are usually between 4 and 9 \AA^2 and the height of their transferred LB films ranges from 25 to 60 \AA , while the theoretical predictions are $(20 \pm 6) \text{ \AA}^2$ and $(7 \pm 3) \text{ \AA}$, respectively (the high dispersion accounting for the different molecular conformations presented by this polymer) [12,34,35,41–43]. In all these cases, the Langmuir and LB monolayers would not be monomolecular layers, but rather single-layers formed by aggregated material. Hydrogen bonding between neighboring chains should be at the origin of the aggregation in these systems, as is found for functionalized fullerenes [18,19]. Compared to LB-polyaniline films [35,41], our LS-PAN films show a much more uniform and smooth surface, although the surface roughness and heights of our films show that they would also be formed by aggregated polymeric chains. The development of high quality and uniform LB-type PAN films with controlled thickness and

ordering degrees should be quite interesting to molecular electronics applications. Thus, we intend to direct further effort toward this end in future investigations.

4. Conclusions

The achievement of Langmuir-type films of poly(5-amino-1-naphthol) on the air/water interface is described. Surface pressure versus molecular area isotherms and hysteresis cycles of the Langmuir PAN films showed very low compressed molecular area and high molecular rearrangement under pressure. PAN single-layer solid films transferred by the Langmuir–Blodgett (vertical lifting) technique onto Si substrate showed a high tendency toward aggregation and low surface coverage of about 40%. On the other hand, the Langmuir–Schaefer (horizontal lifting) method gave high quality, uniform and smooth thin films of about 50 \AA thicknesses, over practically all the substrate. The Langmuir, LB- and LS-PAN films are not monomolecular: molecular aggregation accounts for the observed small molecular area of the Langmuir films and high thickness and roughness of the LB and LS single-layer films.

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