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Research Article

Effect of Salicylic Acid and 5-Sulfosalicylic Acid on UV-Vis Spectroscopic Characteristics, Morphology, and Contact Angles of Spin Coated Polyaniline and Poly(4-aminodiphenylaniline) Thin Films

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Polyaniline and poly(4-aminodiphenyl)aniline have been prepared following two different synthetic protocols (a traditional method and a "green" method). Both the polymers have been spin coated with salicylic acid and 5-sulfosalicylic acid as the dopants, in order to obtain them in form of thin films. These materials have been characterized, thereof achieving important information on their water contact angles and surface morphology.

1. Introduction

Among electrically conducting polymers, polyaniline (PANI) is the most extensively studied thanks to its easy synthesis and unique properties, such as good electrical conductivity and environmental stability [1, 2], which make it particularly appealing for applications in biomedical and technological sectors [3–9]. Even though aniline oxidative polymerization represents the main way towards polyaniline, the scarce processability due to its low solubility in common organic solvents and the poor mechanical properties of the final polymer have encouraged new investigations. Possible synthetic alternatives have emerged consisting in the insertion of long and flexible substituents in the polymer backbone [10], such as alkyl- [11], alkoxy- [12], or *N*-aryl- [13] groups on rings. In this context, we have recently proposed the oxidative polymerization of 4-(aminodiphenyl)aniline (aniline dimer) leading to poly(4-aminodiphenylaniline), P4ADPA, which is a kind of polyaniline [14, 15]. The pioneering investigations of Kitani and Geniès demonstrated that P4ADPA, obtained *via* 4-(aminodiphenyl)aniline oxidative polymerization by stoichiometric oxidants, that is, $(NH_4)_2S_2O_8$, is characterized by polymeric chains shorter than PANI. If on the one hand these latter ensure good solubility in common organic solvents, on the other hand they have a negative effect on conductivity [14, 15]. Starting from these pieces of information and considering our experience in the field of catalysis [16, 17], we recently presented innovative environmentally friendly approaches to produce PANI and P4ADPA [18–23]. In addition, some promising applications were also investigated [24, 25], especially employing PANI and its derivatives as thin conducting films [26, 27]. In this regard, several methods and techniques have been suggested, such as extrusion of a polymer melt, casting of a polymer solution, *in situ* grown films, and electrochemical approaches. Among them, spin coating has emerged as a valid alternative for homogeneous thin films deposition with good optical quality.

However, because of PANI low solubility in organic solvents, its films are generally produced by *in situ* growth syntheses [2, 28, 29] and only a few papers deal with spin coating approach [30].

Herein, we present a spectroscopic investigation of spin coated thin films of salicylic (SA) and 5-sulfosalicylic acid (SSA) doped PANI, prepared following a traditional method, and P4ADPA, prepared by a green approach. Furthermore, the dopants effects on contact angles and surface morphology of the films were also determined and discussed. Salicylic acid was chosen for its anti-inflammatory properties and application in skin-care treatment, whereas 5-sulfosalicylic acid was employed to investigate how the addition of a sulfonic group in the SA structure could modify PANI and P4ADPA properties.

2. Experimental

2.1. Chemical and Instruments. All the chemicals were purchased by Sigma Aldrich and used as received without further purification.

UV-Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer. FT-IR spectra of KBr dispersed samples were recorded by a JASCO FT/IR-410 spectrophotometer in the 500–4000 cm^{-1} range. The molecular weights distribution of the samples soluble fractions was valued by size exclusion chromatography (SEC) using a Shimadzu LC10ADVP HPLC equipped with a refractive index (RI) as the detector. The SEC column was a Phenomenex phenogel 5u 55A (300 $*$ 4.6 mm). Measurements were carried out at room temperature using ultrapure dimethylformamide (DMF) as the eluent. The flow rate was set at 0.3 mL/min and the injection volume was 20 μL. Polystyrene standards were used to calibrate the column.

Thin films were prepared with a Cookson Electronic Company P-6708D spin coater. Films thicknesses, obtained averaging the values measured on 3 different scratches of each film, were measured by a Dektakxt Stylus Profiler profilometer.

Contact angles were measured with 3 μL deionized water droplets by means of a Dataphysics OCA 20 instrument at room temperature. All the contact angles were determined by averaging the values obtained at 2-3 different points on each sample surface. Pictures of the drops were acquired as a function of time, at regular intervals (5 images per second), using the instrument webcam.

2.2. PANI Synthesis. 2 mL of aniline (22 mmol) was added to 719 mL of a 0.3 M HCl aqueous solution (216 mmol) and stirred in an ice bath. Then, 250 mL of a 0.1 M $K_2S_2O_8$ aqueous solution (25 mmol) was added dropwise. After two hours, the ice bath was removed and the reaction mixture was gradually allowed to reach the room temperature. A green solid was collected by filtration after four hours, washed several times with water and acetone to remove organic soluble oligomers, and dried in an oven at 65°C. The product was obtained with 65% yield.

2.3. P4ADPA Synthesis. 5 g of 4-(aminodiphenyl)aniline (27 mmol) was dissolved in 500 mL of a $5.4 \cdot 10^{-1}$ M HCl aqueous solution (270 mmol). Then, 14 mL of H_2O_2 (30% w/w, 135 mmol) was quickly added into the reaction mixture followed by 15 mg of $FeCl_3 \cdot 6H_2O$ (0.055 mmol) at room temperature. After 24 hours, a dark blue-green solid was recovered by filtration, washed several times with deionized water and acetone, and dried in an oven at 65°C. The product was obtained with 52% yield.

2.4. Preparation of Salicylic and 5-Sulfosalicylic Acid Doped PANI and P4ADPA. PANI and P4ADPA, obtained as reported in Sections 2.2 and 2.3, respectively, were separately deprotonated in 300 mL of 0.1 M NH_4OH aqueous solution for 4 hours at room temperature. Then, the products obtained (PANI base, PANI_B, and P4ADPA base, P4ADPA_B) were filtered, washed several times with water until the mother liquor became neutral, and dried in an oven at 65°C.

PANI_B and P4ADPA_B reprotonation with salicylic and 5-sulfosalicylic acid was carried out putting in contact each base with an aqueous solution of these acids, maintaining an aniline/acid molar ratio of 2 (theoretical protonation degree of emeraldine salt, electrically conductive form of polyaniline). Finally, the resulting salts (PANI/SA, P4ADPA/SA, PANI/SSA, and P4ADPA/SSA) were filtered, washed several times with water, and dried in an oven at 65°C.

2.5. Preparation of Thin Films. Polymeric solutions were spin coated onto glass substrates, which were previously subjected to a washing treatment including 3 hours in 6 M HNO_3 at 60°C, followed by several rinses with deionized water and finally acetone. Polymeric solutions were prepared dissolving PANI and P4ADPA powders in DMF at room temperature under stirring overnight. Finally, each solution was filtered.

Thin films were obtained by depositing seven successive layers, using for each one the following spinning parameters: RPM 1 = 700; ramp 1 = 1 s, time 1 = 5 s; RPM 2 = 1000; ramp 2 = 5 s, time 2 = 10 s; RPM 3 = 1000; ramp 3 = 1 s, time 3 = 10 s.

3. Results and Discussion

3.1. Materials Solubility and Molecular Weight Determination by Size Exclusion Chromatography (SEC). All the samples (PANI_B, P4ADPA_B, PANI/SA, P4ADPA/SA, PANI/SSA, and P4ADPA/SSA) were dissolved in DMF. Table 1 reports their solubility values as well as the molecular weight of the soluble fractions of all the materials in DMF, these latter being measured by means of SEC (size exclusion chromatography) technique.

As reported in Table 1 and confirmed by the literature [16], P4ADPA is more soluble than PANI.

It is worth remembering that when polyaniline is protonated with organic acids, such as dodecylbenzenesulfonic acid (DBSA), *p*-toluenesulfonic acid (PTSA), or camphorsulfonic acid (CSA), its solubility grows up [31]. However, in this case, if on the one hand SA and SSA seem to have no strong effect on P4ADPA salts solubility, on the other hand they negatively affect the solubility of PANI-based materials.

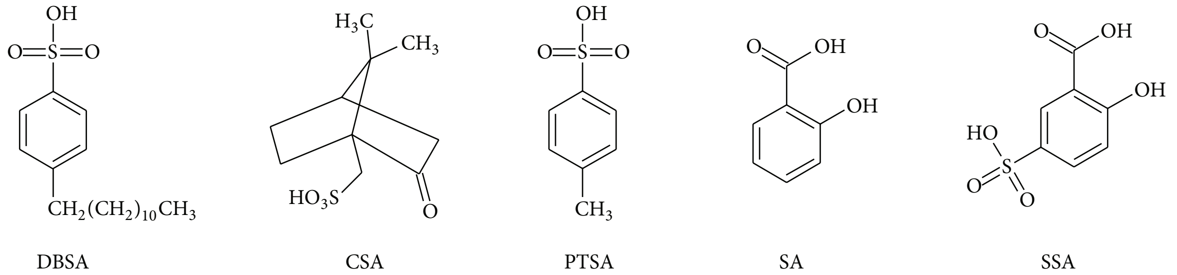


Figure 1: Structure of dodecylbenzenesulfonic acid (DBSA), camphorsulfonic acid (CSA), *p*-toluenesulfonic acid (PTSA), salicylic acid (SA), and 5-sulfosalicylic acid (SSA).

Table 1: Materials solubility in DMF and Mw (weight average molecular weight), Mn (number average molecular weight), and PDI (polydispersity index, Mw/Mn) of soluble fractions as determined by SEC technique.

Sample	Solubility (mg/mL)	Mn	Mw	PDI
PANI_B	2.3	36431	37182	1.02
P4ADPA_B	6.2	85583	152845	1.79
PANI/SA	1.4	7593	12147	1.60
P4ADPA/SA	6.5	12962	67690	5.22
PANI/SSA	1.2	69618	76577	1.10
P4ADPA/SSA	6.3	13443	77026	5.73

This can be due to the smaller dimensions of SA and SSA if compared to other big organic acids (Figure 1).

It has been found that the different solubility values reflect on the thickness of the final films.

In fact, PANI-B films showed a thickness of 360 ± 76 nm, whereas P4ADPA-based films resulted to be thicker, about 880 ± 176 nm. As reported in the literature [32, 33], such a behavior is consistent with the spin coater deposition technique, since the films obtained using the same amount of solvent and spinning parameters have a final film thickness which is directly proportional to the solution concentration.

As reported above, the molecular weight of all the materials was determined by SEC technique using polystyrene standards. However, it should be underlined that polystyrene, PANI, and P4ADPA have different hydrodynamic volumes [34]. Therefore, this technique is considered a secondary molecular weight determination method, leading to values that do not represent absolute molecular weights.

It is worth noting that SA and SSA differently influence the molecular weight distribution of PANI and P4ADPA. Accordingly, although PANI-based materials display narrow polydispersity, PDI, (*ca.* 1), for P4ADPA-based materials the PDI parameter increases from 1.79 up to 5.73 (Table 1). Moreover, from Mw values it is clear that P4ADPA in form of base and salts is characterized by higher molecular weights than those of PANI derivatives.

Despite this, all PANI-based samples turned out to be less soluble than P4ADPA-based ones. Even though the real reason is still not clear, it could be attributed to the presence of branches and/or crosslinking in PANI derivatives.

3.2. UV-Vis Characterization of PANI and P4ADPA Thin Films.

Since polyaniline UV-Vis spectrum can be affected by many factors, such as protonation grade and oxidation states, UV-visible spectroscopy is a useful tool for characterizing PANI and P4ADPA, as well as evaluating the interactions between dopant and polymer chains.

The spectra of PANI_B and P4ADPA_B spin coated films, reported in Figure 2(a), are typical of polyaniline in its emeraldine base form. More in detail, the first peak at about 300 nm can be assigned to the benzenoid rings, whereas the second one at around 550 nm for PANI_B and around 630 nm for P4ADPA_B is due to π-π^* transition of the azaquinoid moieties in the molecule. A different polymeric chains orientation is assumed to be responsible for the shift registered for the second band (550–630 nm), although no literature data can presently support such a hypothesis. Owing to PANI/SA and PANI/SSA low solubility in common organic solvents, it was not possible to realize films of such materials by spin coating technique; therefore only UV-Vis spectra of P4ADPA/SA and P4ADPA/SSA thin films are reported. Furthermore, the band at around 800 nm and the shoulder observed at ca. 430 nm of P4ADPA protonated films (Figure 2(b)) can be assigned to transitions involving polaron states (charged cation radicals), π–polaron, and polaron–π^* transitions.

It is worthy to be highlighted that the doping level of P4ADPA/SSA film resulted to be higher than P4ADPA/SA film although equal amounts of SA and SSA were used to protonate P4ADPA, as confirmed by the ratio of the bands between 600 nm and 800 nm. It is known, in fact, that in UV-Vis spectrum of PANI, but also P4ADPA, the doping process causes a π-π^* transition band shift (*ca.* 600 nm) at higher wavelength values (*ca.* 800 nm). In the spectra reported in Figure 2(b) both the bands can be observed. However, in UV-Vis spectrum of P4ADPA/SSA film the band at 800 nm is higher than the one at 600 nm, thereby suggesting a higher protonation degree of the material probably due to the stronger acidity of SSA than SA for the presence of a sulfonic acid group [35].

All the attempts made to increase P4ADPA/SA protonation degree failed. In this regard, reducing aniline dimer/SA

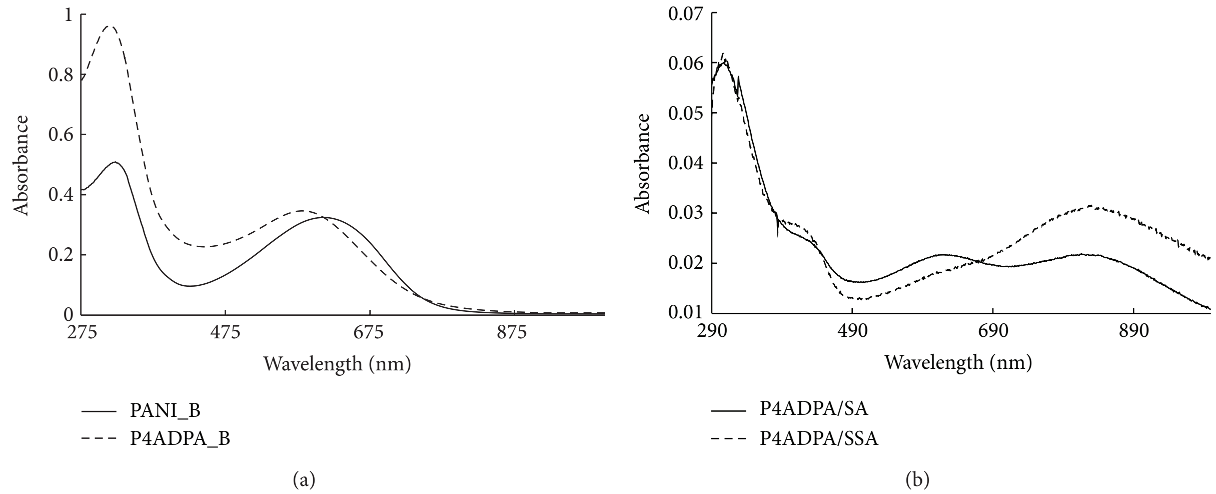


Figure 2: UV-vis spectra of (a) PANI_B and P4ADPA_B and (b) P4ADPA/SA and P4ADPA/SSA thin films.

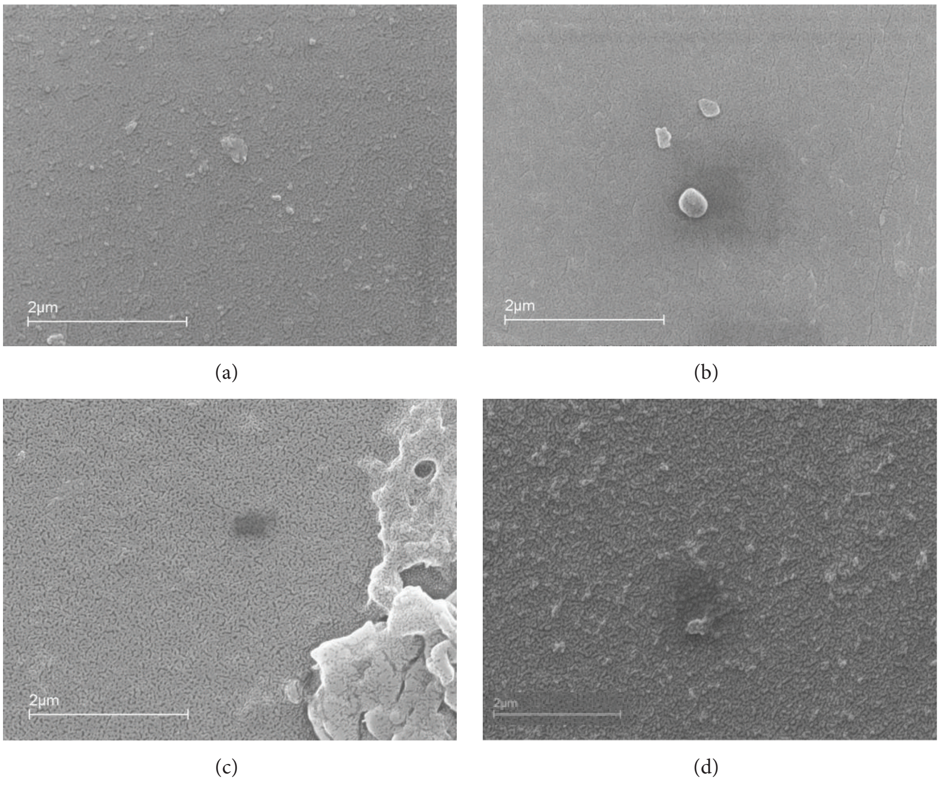
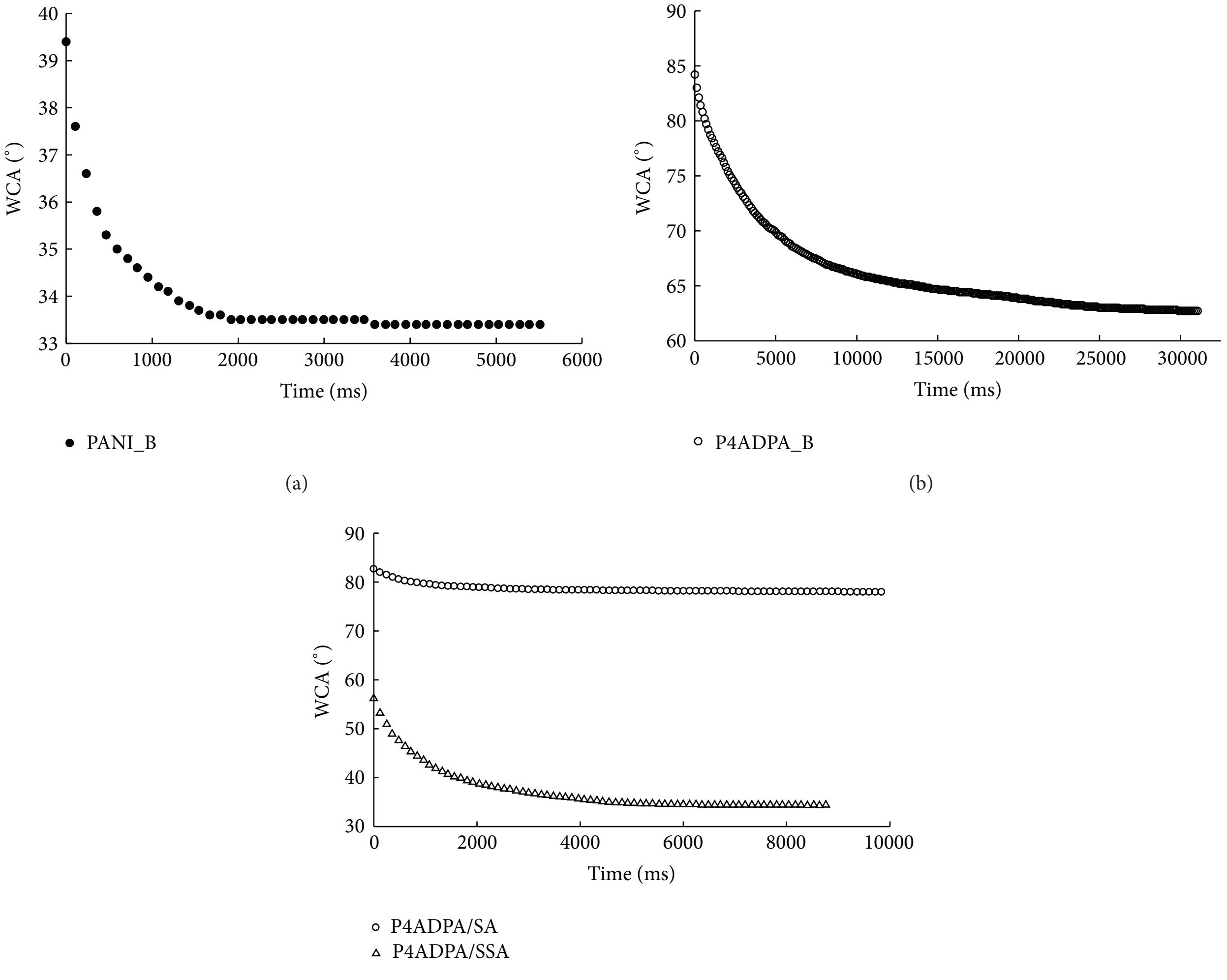


Figure 3: SEM images of (a) PANI_B, (b) P4ADPA_B, (c) P4ADPA/SSA, and (d) P4ADPA/SA.

molar ratio during the materials preparation had a negligible effect on P4ADPA doping level as well as adding further SA amount in the organic solution containing P4ADPA/SA dissolved in DMF. The films obtained following this procedure resulted to be decorated by SA crystals, due to the free acid excess, thus preventing any type of characterization.

3.3. Scanning Electron Microscopy (SEM) Characterization. The surface morphology of PANI_B, P4ADPA_B, P4ADPA/SA, and P4ADPA/SSA films was investigated by scanning electron microscopy whose achievements are reported in Figure 3.

All the samples turned out to be compact and rather homogeneous, even though some irregularity was observed. Although P4ADPA_B seems to be smoother than PANI_B, the differences are not dramatic and could be ascribed to a different polymeric chains arrangement related to the diverse synthetic methods used. However, in its doped form P4ADPA



(a) (b) (c)

Figure 4: Variation of the contact angles measured on PANI_B, P4ADPA_B, P4ADPA/SA, and P4ADPA/SSA with the drop age.

(Figures 3(c)-3(d)) displays a preferential uniform sponge-like morphology. According to the literature [36], the surface morphology differences among P4ADPA base and its salts can be attributed to a big polymeric chains rearrangement owing to chains-ion dopant interactions.

3.4. Water Contact Angle (WCA) Measurements. The contact angle (CA), θ, of a liquid drop on a solid surface is a useful measure of the interactions at the solid-vapor, solid-liquid, and liquid-vapour interface [37]. The surface tension of a material determines its wettability [38]. Typically, high CA values are an indication of low wettability, whereas low CA values correspond to high wettability. Contact angle measurements can be affected by many parameters, such as temperature [39], light [40], roughness [41], and surface morphology [42]. This means that such a property can be handily tuned.

Figure 4 shows the variation of the contact angle with the drop age, measured on the spin coated PANI_B, P4ADPA_B, P4ADPA/SA, and P4ADPA/SSA films.

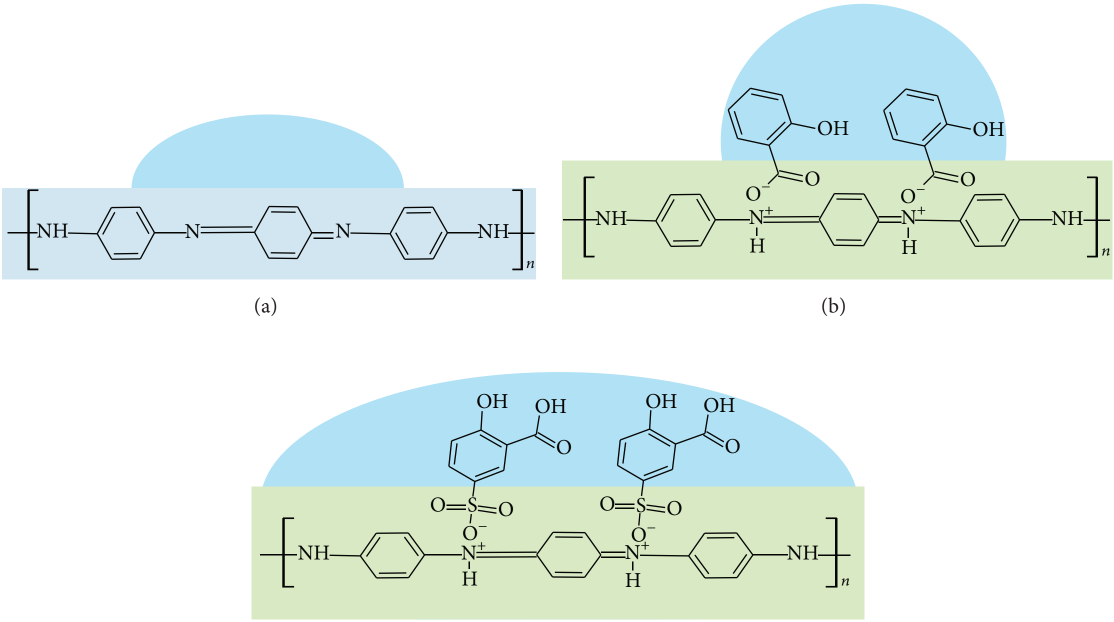
It can be noticed that the contact angle of all the samples decreases with time, probably as a result of a reorientation of the polymeric chains in contact with water which leads to the exposure of hydrophilic groups at the solid/liquid interface. All the contact angles decrease up to equilibrium values, but different samples take different times to reach this equilibrium.

Owing to the absence of strong hydrophilic groups in P4ADPA_B film, its polymeric chains undergo a slow reorganization before reaching the WCA equilibrium value (which is reached in 25 s). On the contrary, this reorganization is almost immediate for P4ADPA/SA (2 s) and P4ADPA/SSA (5 s) films, thanks to the presence of hydrophilic groups in SA and SSA dopants.

Equilibrium values of contact angle measured on different samples are reported in Table 2.

As reported in the literature, PANI is characterized by values of WCA < 90° and its hydrophilicity can be tuned by using proper dopants [43, 44].

The WCA value of PANI_B film was unexpectedly low since for polyaniline in its emeraldine base form higher



(a)

(b)

(c)

Figure 5: Proposed mechanism for the wettability observed for (a) P4ADPA_B, (b) P4ADPA/SA, and (c) P4ADPA/SSA films.

Table 2: Equilibrium values of contact angle measured on PANI_B, P4ADPA_B, P4ADPA/SA, and P4ADPA/SSA films.

Sample	WCA (°)
PANI_B	33.4
P4ADPA_B	62.7
P4ADPA/SA	78.0
P4ADPA/SSA	34.6

values are generally reported. Liu et al. [45] and Shishkanova et al. [46] reported 84° and 94° WCA, respectively. The extraordinary low WCA value for PANI_B film observed in the present study could be related to the presence of impurities, such as traces of NH_4OH and sulfates, deriving from the synthetic process.

In the case of P4ADPA-based films, the WCA values resulted to be strictly connected to the presence and type of the acid dopant. Accordingly, P4ADPA film in its base form showed a WCA of 62.7°. However, when SA was used as the doping agent, WCA slightly increased reaching the equilibrium value of 78.0°, whereas this dramatically dropped down to 34.6° in the case of P4ADPA/SSA film.

In order to explain such a trend, a mechanism focused on the role of the dopant is suggested (Figure 5).

Starting from the WCA value of P4ADPA_B, when the material is doped with salicylic acid the exposure of the benzenic rings on the surface can cause a reduction of hydrophilicity with a resulting increase of WCA (78.0°C). On the contrary, the presence of hydrophilic chemical groups (–OH and –COOH) on the SSA ring might be responsible for the low WCA value of P4ADPA/SSA film. IR and Raman investigations are in progress in order to confirm such a supposed mechanism.

4. Conclusions

Films of PANI and P4ADPA as either bases or salts, doped with salicylic acid (SA) and 5-sulfosalicylic acid (SSA), were prepared by spin coating procedure. Size exclusion chromatography (SEC) revealed that even though common organic acids, such as *p*-toluenesulfonic acid, dodecylbenzenesulfonic acid, or camphorsulfonic acid, typically confer positive effects on PANI and P4ADPA solubility in organic solvents, salicylic acid and 5-sulfosalicylic acid had no effect on P4ADPA solubility while reducing the solubility of PANI-based materials. These achievements can be attributed to the small dimensions of SA and SSA. UV-Vis spectroscopic investigations showed SSA to lead to a complete protonation of the imine groups of P4ADPA, due to the presence of a sulfonic group allowing interactions with the polymer stronger than those of carboxylic group. In fact, in the presence of SA only a partial protonation of P4ADPA films was observed. Moreover, the presence of dopants causes a surface morphology change of P4ADPA films from smooth, in the case of P4ADPA base, to sponge-like texture for P4ADPA in form of salt. This modification was ascribed to chains rearrangement caused by interactions with the dopant. Finally, water contact angles turned out to be strongly affected by the presence and type of organic acid, thus suggesting a mechanism for the materials wettability herein presented.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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