

## Interfacial Polymerization of Polyaniline and its Layer-by-Layer Assembly into Polyelectrolytes Multilayer Thin-Films

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**ABSTRACT:** The layer-by-layer (LbL) self assembly deposition technique was used to prepare multilayer thin films of anionic polyaniline-blend-poly(sodium 4-styrenesulfonate) (PANI-PSS) and cationic poly(diallyldimethylammonium chloride) (PDADMAC). Anionic polyaniline was prepared by the interfacial polymerization of aniline monomer in the presence of PSS which acted as template to provide water solubility. The PSS to PANI concentration ratios used in the synthesis step was found to have a major effect on the final PANI-PSS synthesis, its self assembly and the electrical properties of the prepared films. The optical and electrical properties of the films were measured by ultraviolet-visible spectroscopy (UV-Vis) and a 4-point probe setup, respectively while the thickness of the films was measured by atomic force microscopy (AFM). Results showed that the optimum condition for the film growth and optimal conductivity were obtained with different synthesis conditions. These results suggest that the PSS concentration used for interfacial synthesis of PANI must be finely tuned depending on the type of application aimed by the user. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** water-soluble polyaniline; interfacial polymerization; layer-by-layer (LbL); polyelectrolyte multilayers

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### INTRODUCTION

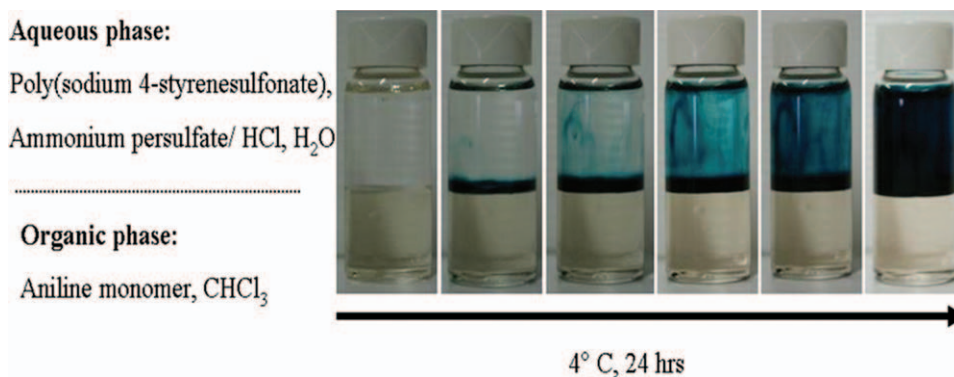
Development in the fabrication of ultra-thin films composed of conducting polymer having defined architectures are used mainly for flexible electrodes in materials such as organic solar cells or organic light emitting diodes. These organic-electronic materials are used for their remarkable mechanical<sup>1</sup> and electrical properties,<sup>2</sup> which can be exploited in various application such as electronic component,<sup>3</sup> sensors,<sup>4</sup> electromechanical actuators,<sup>5</sup> displays,<sup>6</sup> smart windows,<sup>7</sup> and membrane.<sup>8</sup> Various techniques for the fabrication of well-defined thin conducting films have been proposed such as spin-coating,<sup>9</sup> chemical vapor deposition,<sup>10</sup> or langmuir-blodgett technique<sup>11</sup> but require fairly expensive equipment or are limited to the production of flat samples. On the other hand, interest in the so called layer-by-layer (LbL) self assembly has increased dramatically since Decher et al.<sup>12</sup> reintroduced the multilayering procedure for thin film fabrication based on the electrostatic interaction between positive and negative charges of macromolecules. The LbL self assembly deposition technique has become an attractive method for the fabrication of conducting polymer thin films because its procedure is simple, does not require any organic solvent and only small amount of chemicals are used.<sup>13</sup>

Polyaniline (PANI) is an interesting class of conducting polymer that exhibit conductivity changes upon redox,<sup>14</sup> has good envi-

ronmental stability,<sup>15</sup> is simple to synthesize,<sup>16</sup> is fairly inexpensive,<sup>17</sup> and has a stable electrical conductivity.<sup>18</sup> PANI is usually soluble in nonpolar solvent and therefore, insoluble in water, which to some extent, restricts its application for the LbL self assembly. Efforts have been made toward overcoming such limitations and one approach was to introduce functional groups such as  $-\text{COOH}$ ,<sup>19</sup>  $-\text{SO}_3\text{H}$ <sup>20</sup> along the PANI chains by acidic treatment. Using this strategy, PANI can be prepared and deposited into thin films using the LbL technique as proposed by Sarkar et al.<sup>21</sup> using sulfonated PANI (PANI- $\text{SO}_3\text{H}$ ) with the positive charges poly(diallyldimethylammonium chloride) (PDADMAC) polyelectrolyte. Travas-Sejdic and coworkers<sup>22</sup> also demonstrated an electrostatic self assembly of PANI thin films on LbL using poly(*o*-methoxyaniline) with poly(styrene sulfonic acid). This method is interesting but the acidic treatment can make the process difficult to scale up and other possibilities were investigated. Recently, the doping of PANI with negatively charged polyelectrolyte such as poly(acrylic acid),<sup>23</sup> poly(vinyl sulfonate),<sup>24</sup> or poly(sodium 4-styrenesulfonate) (PSS)<sup>25</sup> in the so called interfacial polymerization was proposed. In this method, water-soluble template anionic polyelectrolytes are used to provide water solubility to aniline in a chloroform phase. The aniline monomer polymerizes and transfer to the aqueous

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**Figure 1.** Diagram depicting the interfacial synthesis of polyaniline with PSS as template. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

phase by binding with the polyanionic polymer. This very simple method to synthesize water-soluble PANI is receiving great interest but no reports have been made of their LbL self assembly into polyelectrolyte multilayers.

This article describes the possibility of the fabrication of PANI thin film by LbL self assembly technique and the effect of the PSS concentration used in the synthesis on the final electro-optical properties of the film. Water-soluble Polyaniline was prepared by interfacial polymerization of aniline monomer in the presence of anionic PSS and poly(diallyldimethyl ammonium chloride), PDADMAC was used as the polycationic species. The films were characterized for their optical and electrical properties using ultraviolet-visible (UV-Vis) spectroscopy and a 4-point probe setup, respectively. The thickness and surface of the film was measured by atomic force microscopy (AFM).

## EXPERIMENTAL SECTION

### Chemicals

Aniline monomer ( $C_6H_5NH_2$ ), ammonium persulfate (APS),  $(NH_4)_2S_2O_8$ , chloroform ( $CHCl_3$ ), hydrochloric acid (HCl), sodium chloride (NaCl), (poly(sodium 4-styrenesulfonate) (PSS), molecular weight = 70,000), and (PDADMAC, molecular weight = 200,000/350,000) were purchased from Aldrich Chemicals, Thailand. All chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with Deionized water (DI).

### Polyaniline Synthesis

Water-soluble polyaniline was prepared by interfacial polymerization in the presence of PSS. The experiment was performed into two phases of aqueous and organic solution (chloroform) with the aqueous phase composed of PSS and APS with HCl and the aniline monomer dissolved in  $CHCl_3$ . Different aniline monomer:PSS ratios were used (10 : 3, 10 : 5, 10 : 10, 10 : 20, 10 : 50, 10 : 100, 10 : 150 and 10 : 200 mM) while the APS was fixed at 5 mM and 1 M HCl. The aqueous phase had a volume of 100 mL in the organic phase 30 mL. A green water-soluble polyaniline was formed at the interface within a few minutes. The reaction solution was kept without agitation for 24 h, 4°C. Once completed the aqueous solution was separated from the organic solution and used in the LbL experiments.

### LbL Film Assembly

PANI-PSS prepared from different aniline:PSS ratios were each deposited with PDADMAC. Each substrate was first coated with a 5 layers of PDADMAC/PSS which acted as a primer to insure good build up of the PDADMAC-PANI films. The pH of all the PANI-PSS solutions was adjusted to a value of 6. The LbL deposition method has been described previously and in our experiments, the dipping time was 5 min in each polyelectrolyte and three rinses in DI water of 3 min after each layer.

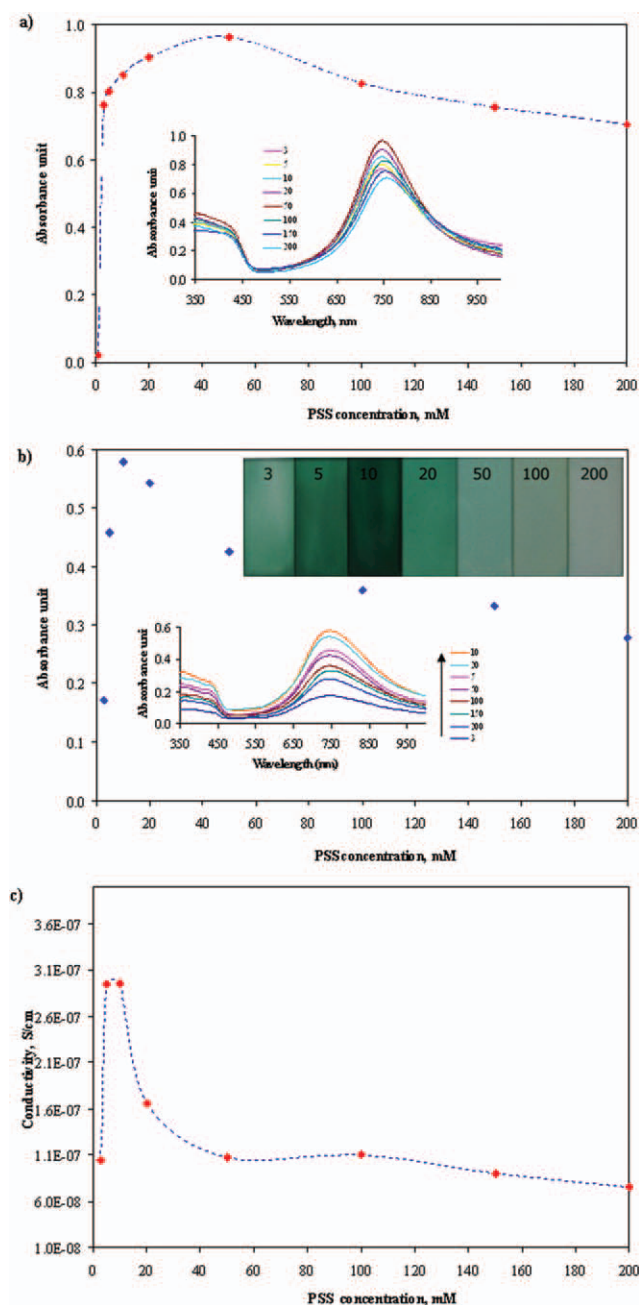
### Characterization

The optical properties of the polyaniline films deposited on the glass substrates were measured using UV-Vis spectroscopy (Specord S100, Analytikjena spectroscopy). The fourier transform infrared (FTIR) spectra were acquired with Spectrum One, Perkin Elmer. The morphology of polyaniline was characterized by transmission electron microscope, JEOL-JEM-2100. The zetasizer (NanoZS4700 nanoseries, Malvern Instruments, UK) was used to measure the surface zeta potential of the PANI-PSS solution with different pH. The electrical properties of polyaniline films were measured with a 4-point probe setup and the thickness and surface of the films were measured by AFM (NanoScope IV, Veeco) in tapping mode using a silicon tip.

## RESULTS AND DISCUSSION

### Interfacial Polymerization of Polyaniline

PSS was used as a template to provide water-soluble properties to PANI through the interfacial synthesis. In this system, PANI has been shown to form at the interface of the two solvents (water/chloroform) within a few min, producing a green solution in the aqueous phase as seen in Figure 1. In the absence of PSS in the aqueous phase, PANI can be formed but remains at the interface in the form of precipitated green particles. The interfacial polymerization has been studied in number of research papers which concluded that a 4°C reactor, 1 M HCl concentration, and an excess of PSS provided the optimum conditions for the polymerization of PANI. In these experiment, PSS was used in excess to maximize the template effect of the PSS on PANI and improve its solubility which unfortunately also leads to unreacted PSS excess in solution which can be a limiting factor for the LbL deposition of PANI-PSS for example



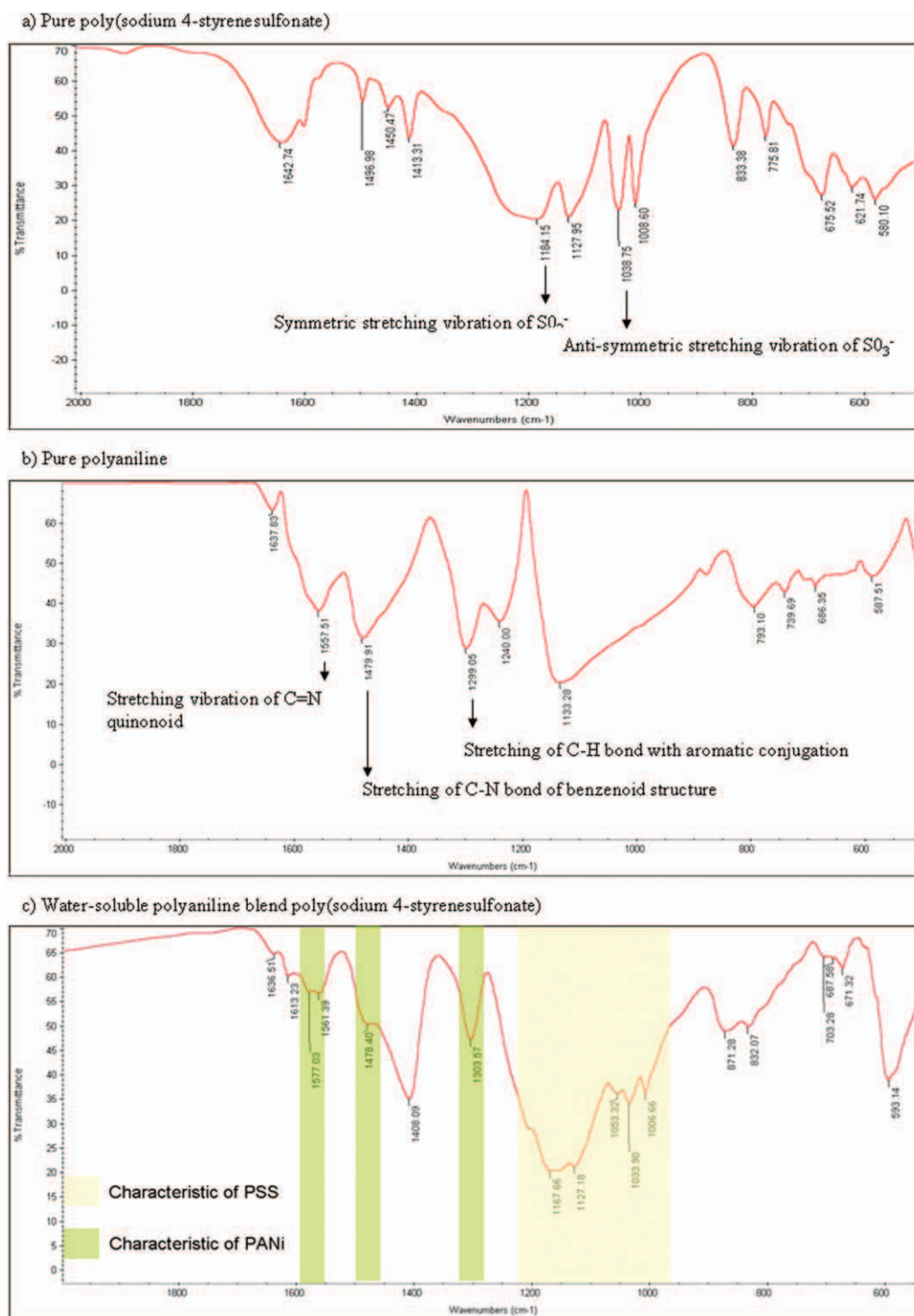
**Figure 2.** (a) Plot of the change in absorbance of the aqueous phase after interfacial polymerization as a function of PSS concentration. (b) Plot of the change in absorbance of glass slide coated with 13 layers of (PANI-PSS/PDADMAC) multilayer films as a function of the PSS concentration used in the synthesis step. (c) The changes in conductivity of 21 layers (PANI-PSS/PDADMAC) multilayer films at various concentration feed ratio of PANI-PSS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

with cationic PDADMAC. Our main motivation in this work was to study the effect of the PSS concentration first on the synthesis and second on the film growth. When PANI-PSS was prepared with a PSS concentration above 3 mM, the aqueous phase quickly turned green. It is expected that a minimum concentration of PSS is needed to disperse the polymerized

PANI with PSS as a template<sup>26</sup> but when the PSS concentration is lower than 3 mM, the PANI precipitate at the interface. UV-Vis absorbance of the PANI solutions at 750 nm was found to increase with increasing PSS concentration from 3 to 50 mM but decreased when the PSS concentration was over 100 mM as shown in Figure 2(a). As suggested in previously published work, strong electrostatic interaction between  $-\text{SO}_3^-$  groups of PSS and  $(-\text{NH}_3^+)$  groups of polyaniline backbone as well as the  $\pi$ - $\pi$  interactions between the benzene rings on PSS and aniline are responsible for the templating effect of PSS over PANI.<sup>26</sup> The anilinium cation can absorb completely through the electrostatic interaction onto a large amount of sulfonic groups of PSS. The decrease in absorbance for high PSS concentration (100 and 200 mM) suggests a slower polymerization rate due to the high viscosity of the PSS solutions.<sup>26</sup> To further confirm this assumption, 500 mM PSS was used in the synthesis of PANI and the UV-Vis absorbance was found to further decrease (corresponding data are available in the Supporting Information of this article). FTIR was used to analyze the functional groups of each compound after synthesis. These were compared to the FTIR spectra of pure PSS [Figure 3(a)] and pure polyaniline [Figure 3(b)]. The FTIR spectrum of PSS shows a characteristic peak at  $1,184\text{ cm}^{-1}$  and  $1,037\text{ cm}^{-1}$  for the symmetric-stretching and antisymmetric-stretching vibration of  $-\text{SO}_3^-$  groups, respectively. The peak at  $1,127\text{ cm}^{-1}$  and  $1,008\text{ cm}^{-1}$  are attributed to in-plan skeleton vibration and in-plan bending vibration of the benzene ring, respectively.<sup>25</sup> In the FTIR spectra of pure polyaniline, the absorption peak observed at  $1557$ ,  $1479$ , and  $1299\text{ cm}^{-1}$  corresponding to the stretching of  $\text{C}=\text{N}$  bond of quinoid structure, the stretching of the  $\text{C}-\text{N}$  bond of benzenoid structure and the stretching of the  $\text{C}-\text{H}$  bond with aromatic conjugation, respectively. All characteristic absorbance peaks of pure PSS and pure polyaniline can be observed in the FTIR spectra of water-soluble polyaniline-blend PSS as can be seen in Figure 3(c). The main characteristic absorption peaks of  $\text{SO}_3^-$  group are visible at  $1,184\text{ cm}^{-1}$  and  $1,037\text{ cm}^{-1}$  demonstrating the polymerization of polyaniline. The morphology of the PANI-PSS polymer was observed by transmission electron microscopy (TEM) and pictures are shown in Figure 4. The TEM pictures show that a elongated shape particles of about 600–800 nm in diameter are obtained. The size of PANI particle appear larger when compared with data reported by other groups.<sup>25,21</sup> Wen and Kuo<sup>25</sup> who reported the PANI particle size of about 20–200 nm when using high PSS concentrations. They also reported that the particle size increased with decreasing PSS concentration which correspond to our case as we are using lower capping concentration in order to reduce the excess PSS in solution. At this point, the optimal concentration for PSS appeared to be 50 mM as it gave the highest absorbance and therefore the highest yield.

### Polyelectrolyte Multilayer Films Fabrication

An interesting point was to know whether the optimum PSS concentration (50 mM) for the synthesis of PANI-PSS would also be the best condition for the LbL film growth. When using high PSS content, the excess of unreacted and unbonded PSS cannot be separated neither by dialysis tube nor centrifugation and remains in solution with the PANI-PSS polymer. This



**Figure 3.** FTIR spectra of (a) PSS (b) pure polyaniline and (c) polyaniline-blend-PSS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

appeared quickly to be a limitation for the film growth. Films were prepared by depositing 13 layers of PDADMAC and PANI-PSS prepared from various concentration of PSS in the feed solution. The absorbance at 750 nm of each film was recorded and plotted in Figure 2(b). It can be seen that in the case of the film, the maximum absorbance was obtained for PANI-PSS sol-

utions prepared from 10 mM PSS. Films assembled from higher PSS content 20 to 200 mM showed a lower absorbance due to the expected competition between the excesses of PSS remaining in solutions and the PANI-PSS as proposed earlier in the paragraph. Based on UV-Vis absorbance measurements, the 10 mM PSS can be identified as the best condition for the film

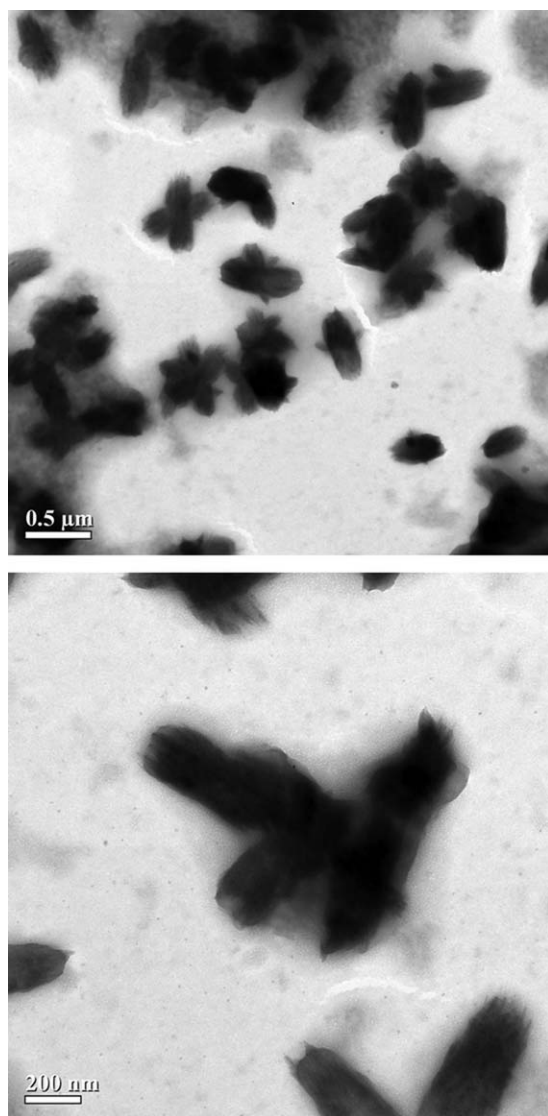


Figure 4. TEM images of polyaniline-blend-PSS.

growth. AFM was used to correlate the absorbance maximum with the film thickness by scratching the surface of thin film with a sharp tool in order to create a step edge. Then the AFM tip can be placed on the edge and an AFM image of the cross section can then be taken for analysis. The measured thickness, roughness, and AFM images are compiled in Figure 5. It can be seen that the film thickness also presented a maximum for 10 mM PSS solutions as it was found in the UV-Vis plot [Figure 2(b)]. The morphology and smoothness of (PANI-PSS/PDADMAC) multilayer films at the different PSS concentration was also investigated. The AFM images shown in Figure 6 present the surface topography of the (PANI-PSS/PDADMAC) multilayer films at 13 layers. The RMS values of each AFM images at 3, 5, 10, 20, and 50 mM of PSS concentration was calculated to be 15.93, 20.13, 54.55, 5.84, and 4.51 nm, respectively. It can be seen again that the 10 mM condition provide the rougher films. The lower values 15.93 nm and 20.13 nm are due to the thinner films when the PSS concentration is too low to insure the film

growth. The lower roughness values for higher PSS content are due to smaller PANI particles size.

Because our goal was to produce thin films of PANI-PSS having the highest conductivity possible, the same question throughout our work was to know if the thicker films prepared from 10 mM PSS would have the best conductivity. Four-point probe measurements were used to measure the conductivity of each films by measuring the voltage drop across the inner two electrodes while the current between the outer electrodes was fixed. As shown in Figure 2(c) the highest conductivity was obtained between 5 and 10 mM PSS because the low PSS capping allows strong interaction between the PANI branches. On the other hand, the high PSS content has a large amount of unreacted PSS which upon adsorption isolate the PANI conductive stand from one another and result in a film having poor conductivity. It is interesting to note that throughout this study, what appeared the best condition for a given experiment from synthesis, film assembly, and conductivity measurement was not the best condition for the following step. Although the interfacial polymerization is very fast and simple for the production of water-soluble PANI, great care must be given to the PSS content as it has a strong effect on the film assembly and resulting electrical conductivity.

#### Parameter Controlling LbL Growth

The LbL film growth as a function of the pH, ionic strength, and number of layers of the solution was also investigated. These three fundamental parameters are usually studied when a new type of polyelectrolyte multilayer (PEM) thin film is proposed. NaCl concentration is an interesting parameter because it can increase the growth rate of the film by screening the repulsion between polyelectrolytes. Changing the pH of the solution effects the ionization of polyelectrolytes changing their conformation and adsorption. The number of layer is the most straight forward parameter as it only confirms that the thickness increases as a function of the number of layers. This increase in thickness has been reported to be linear or exponential for different polyelectrolyte system.

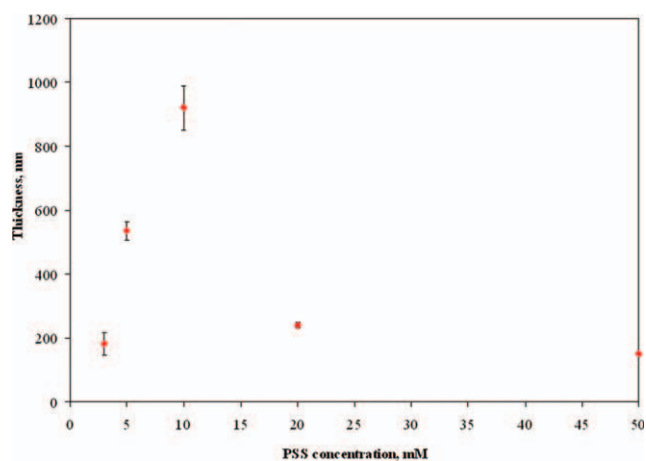


Figure 5. Thickness of (PANI-PSS/PDADMAC) multilayer films as the function of the PSS concentration used in the synthesis step. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

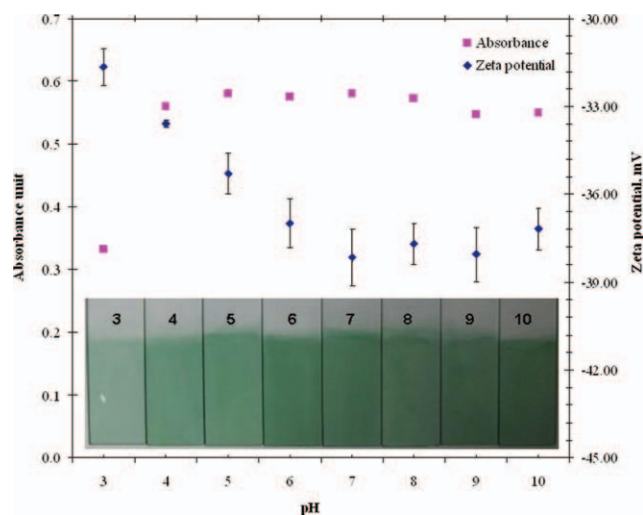
PSS concentration, mM	Morphological Evolution		RMS roughness, nm
	Two-dimensional (scanned at 1 $\mu\text{m}$ )	Three-dimensional (scanned at 5 $\mu\text{m}$ )	
3			15.93
5			20.13
10			54.55
20			5.84
50			4.51

**Figure 6.** AFM images of (PANI-PSS/PDADMAC) multilayer films as the function of the PSS concentration used in the synthesis step. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Shown in Figure 7 are plotted the effect of pH in PANI-PSS solution onto the assemblies of polymer thin films as the function of zeta potential and absorbance of the multilayer thin film versus pH. The absorbance of the PANI thin film was found to increase when the pH was increased from 3 to 5 yet further increase pH of PANI-PSS solution from 5 to 10 did not induce any changes in absorbance. These results can be understood by considering the surface charge of the PANI-PSS in solution which can be estimated by measuring its zeta potential. The polymerized PANI-PSS were found to have the zeta potential values ranging from  $-31$  to  $-39$  mV when the pH increased

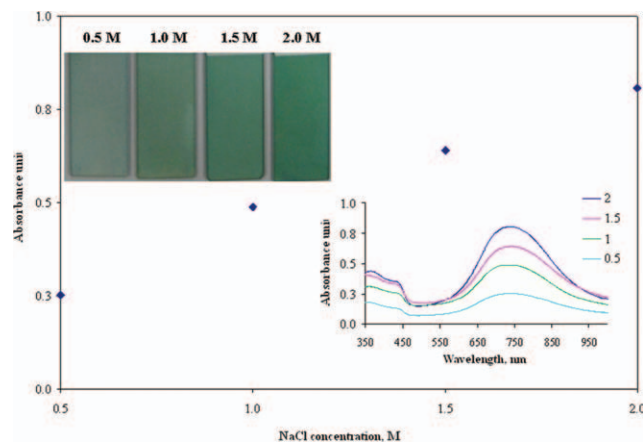
from 3 to 10. The negative zeta potential values are due to the PSS template which confirm the PANI-PSS polymerization. The lower zeta potential for pH values of 3 to 5 are the result of changes in the degree of ionization of the amine or imine groups of PANI. On the other hand, the zeta potential of pH 6–10 was found to stable due to the complete ionization of PANI-PSS.

The plot of the absorbance as the function of NaCl concentration is shown in Figure 8. The experiment was carried out by fixing the number of layer to 9 and varying the ionic strength of the solution from 0.5 to 2 M NaCl. As expected, the final thickness of the film is nearly linearly dependant to the NaCl

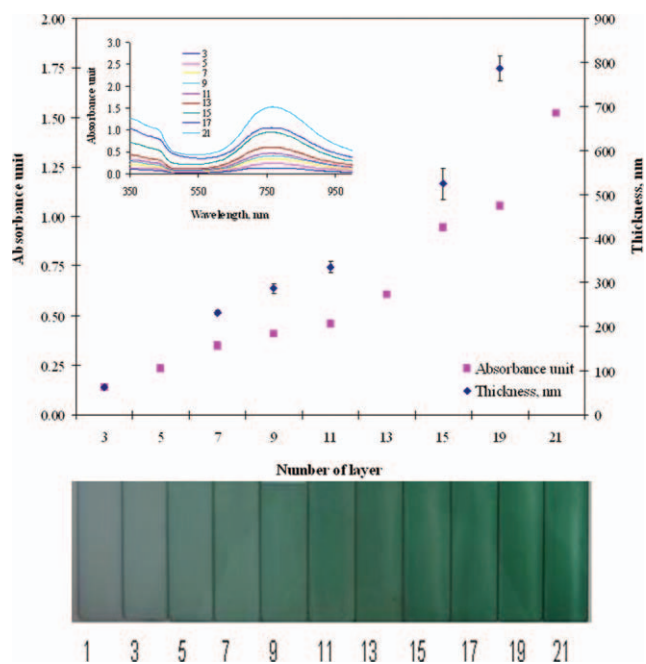


**Figure 7.** Effect of pH in PANI-PSS solution onto the assemblies of (PANI-PSS/PDADMAC) multilayer films, (■) The absorbance value as the function of pH and (◆) Zeta potential as the function of pH and insert picture show the digital images of PANI-PSS films at various pH 3–10 when fix the number of layer at 11. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentration with films appearing greener as NaCl content was increased. The growth of the PANI-PSS multilayers was monitored by AFM and UV-Vis spectroscopy as a function of the number of layers and can be seen to be linear in Figure 9, confirming the LbL step growth of uniform amount for each layer. In Figure 10, the electrical conductivity of each multilayer films is presented and can be seen to be increased with increasing the number of layer. The 19 layers had a conductivity  $3.7 \times 10^{-7}$  S/cm after doping in 1.0 M HCl for 2 h. This was a direct result of the conversion of the emeraldine base form to the emeraldine salt form, which is a highly  $\pi$ -conjugated system.



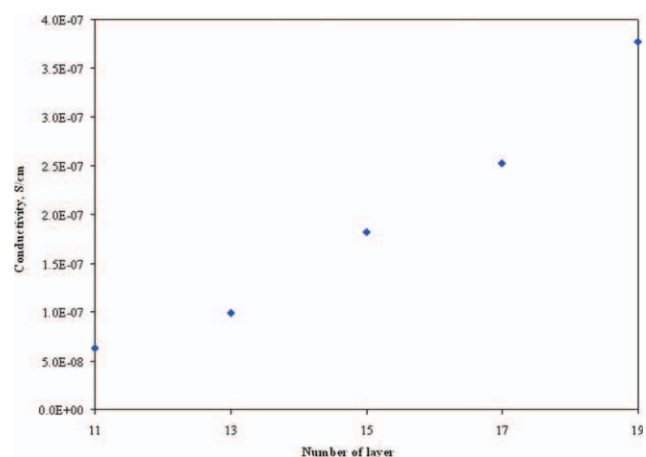
**Figure 8.** Effect of NaCl concentration in PANI-PSS solution onto the assemblies of (PANI-PSS/PDADMAC) multilayer films, insert graph show the picture of PANI-PSS films at various NaCl concentration of 0.5, 1.0, 1.5, and 2.0 M when fix the number of layer at 9. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 9.** The thickness and absorbance value as the function of number of (PANI-PSS/PDADMAC) multilayer films and the representative digital images of assembled (PANI-PSS/PDADMAC) multilayer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## CONCLUSION

The LbL self assembly of PANI-PSS was studied and optimized to produce the best conducting films possible. Results showed that the polymerization and self assembly of PANI-PSS was optimum for 50 mM and 10 mM PSS respectively. The synthesis and self assembly of PANI-PSS methods are very simple but the concentration ratio of PSS to PANI need to be tuned depending on the final utilization. Thickness measurement and TEM image of the film suggest that the particle formed at 5 mM PSS are relatively large but provide the best electrical conductivity. For



**Figure 10.** The conductivity of (PANI-PSS/PDADMAC) multilayer films at various number of layer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the LbL deposition, the optimum conditions were solution with a pH of 6 with ionic strength adjusted with 2 M NaCl. The simple interfacial polymerization technique has been tuned and studied to produce the best LbL growth of conjugated thin films.

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#### REFERENCES

1. Shaktawat, V.; Saxena, N. S.; Sharma, K. *Phase Transit.* **2011**, *84*, 215.
2. Price, A. D.; Naguib, H. E. *Cell. Polym.* **2008**, *27*, 201.
3. Matienzo, L. J.; Das, R. N.; Egitto, F. D. *J. Adhes. Sci. Technol.* **2008**, *22*, 853.
4. Kumar, D.; Gupta, N.; Sharma, S.; Mir, I. A. *J. Sci. Ind. Res. India* **2006**, *65*, 549.
5. Lu, W.; Norris, I. D.; Mattes, B. R. *Aust. J. Chem.* **2005**, *58*, 263.
6. Somani, P.; Mandale, A. B.; Radhakrishnan, S. *Acta Mater.* **2000**, *48*, 2859.
7. Jelle, B. P.; Hagen, G. *Sol. Energ. Mat. Sol. C* **1999**, *58*, 277.
8. Sairam, M.; Loh, X. X.; Bhole, Y.; Sereewatthanawut, I.; Li, K.; Bismarck, A.; Steinke, J. H. G.; Livingston, A. G. *J. Membr. Sci.* **2010**, *349*, 123.
9. Verma, D.; Dutta, V. *Sens. Lett.* **2009**, *7*, 143.
10. Cho, J.; Shin, K. H.; Jang, J. *Thin Solid Films* **2010**, *518*, 5066.
11. Prabhakar, N.; Matharu, Z.; Malhotra, B. D. *Biosens. Bioelectron.* **2011**, *26*, 4006.
12. Decher, G.; Eckle, M.; Schmitt, J.; Struth, B. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 32.
13. Voegel, J. C.; Decher, G.; Schaaf, P. *Actual Chimique* **2003**, *30*.
14. Mu, S. L. *Synth. Met.* **2010**, *160*, 1931.
15. Zhang, F.; Halverson, P. A.; Lunt, B.; Linford, M. R. *Synth. Met.* **2006**, *156*, 932.
16. Kanwal, F.; Gul, A.; Jamil, T. *J. Chem. Soc. Pakistan* **2007**, *29*, 553.
17. Ameen, S.; Akhtar, M. S.; Husain, M. *Sci. Adv. Mater.* **2010**, *2*, 441.
18. Zhang, K. Q.; Li, Y. *Polym. Adv. Technol.* **2011**, *22*, 2084.
19. Kim, S. C.; Whitten, J.; Kumar, J.; Bruno, F. F.; Samuelson, L. A. *Macromol. Res.* **2009**, *17*, 631.
20. Lee, J. H.; Bhadra, S.; Kim, N. H. *J. Appl. Polym. Sci.* **2010**, *117*, 2025.
21. Sarkar, N.; Ram, M. K.; Sarkar, A.; Narizzano, R.; Paddeu, S.; Nicolini, C. *Nanotechnology* **2000**, *11*, 30.
22. Zhang, L. J.; Peng, H.; Hsu, C. F.; Kilmartin, P. A.; Travas-Sejdic, J. *Nanotechnology* **2007**, *18*.
23. Ho, C. H.; Liu, C. D.; Hsieh, C. H.; Hsieh, K. H.; Lee, S. N. *Synth. Met.* **2008**, *158*, 630.
24. Mafe, S.; Manzanares, J. A.; Reiss, H. *J. Chem. Phys.* **1993**, *98*, 2408.
25. Wen, T. C.; Kuo, C. W. *Eur. Polym. J.* **2008**, *44*, 3393.
26. Hopkins, A. R.; Sawall, D. D.; Villahermosa, R. M.; Lipeles, R. A. *Thin Solid Films* **2004**, *469*, 304.