

## Interfacial Polymerization of Water-Soluble Polyaniline and Its Assembly Using the Layer-By-Layer Technique

Ekarat DETSRI<sup>1</sup>, Stephan THIERRY DUBAS<sup>2\*</sup>

<sup>1</sup>Graduate School of Nanoscience and Technology, Chulalongkorn University,  
Phyathai Rd., Bangkok 10330, Thailand

<sup>2</sup>Metallurgy and Materials Science Research Institute, Chulalongkorn University,  
Phyathai Rd., Bangkok 10330, Thailand

### Abstract

Received Apr. 27, 2009

Accepted May 12, 2009

The interfacial polymerization of aniline has been used to prepare water-soluble polyaniline. Polyaniline was made water-soluble by interfacial polymerization in the presence of poly(styrene sulfonated, sodium salt) (PSS), which acted as bundling agent to provide water solubility. The prepared polymer composite was later used for the fabrication of polyaniline nano-thin films using the layer-by-layer (LbL) self-assembly technique. Film produced by the LbL technique can be used in electro-chromic films, sensors or electro-catalytic films depending on the type of architectures. This paper first presents, a brief review on conducting polymer prepared by interfacial polymerization. Special interest is given to the synthesis of water-soluble polyaniline by interfacial polymerization in the presence of PSS. In a second part, the authors provide original results concerning the LbL self-assembly of polyaniline into nano-thin films. The PSS concentration used in the polyaniline synthesis is discussed regarding its effect on the growth of LbL composite thin films.

**Key words** : Polyaniline, Interfacial polymerization, Layer-by-layer

### Introduction

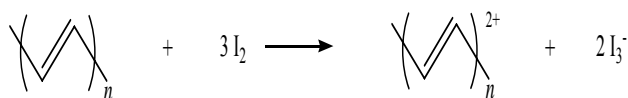
Conducting polymers have received much attention due to their potential usage in several applications such as biosensor,<sup>(1)</sup> electrochemical display,<sup>(2)</sup> corrosion protection,<sup>(3)</sup> or even rechargeable batteries<sup>(4)</sup>. Polyaniline is a type of conducting polymer which received the most attention due to the discovery of its high electrical conductivity,<sup>(5)</sup> reversible acid-base chemistry in aqueous solution, thermal and environmental stabilities and easiness of synthesis.<sup>(6)</sup> Among all the methods which can be used for the synthesis of polyaniline such as oxidative synthesis, electro-polymerization or UV polymerization, the interfacial synthesis of polyaniline is a new and powerful method for synthesis of the water-soluble conducting polyaniline. This advantage is due to the ease of preparation and its fast reaction.<sup>(7)</sup> Furthermore, the usage of anionic polymer in the interfacial polymerization results in a bundled structure which can present a strong affinity for cationic polymer. Thus, the fabrication of polyaniline nano-thin film with LbL self-assembly technique is possible.<sup>(8)</sup> In this paper, an overview of the recent advance in the interfacial polymerization of water-soluble polyaniline is reported. Also original results on

the synthesis of polyaniline bundled with PSS and its assembly in nano-thin films by using LbL self-assembly technique are put forward.

### Materials and Experimental Procedures

#### Conducting Polymer

Conducting polymers were first discovered in 1976 by MacDiarmid, Shirakawa and Heeger, when they found that the conductivity of polyacetylene increased by up to 6 orders of the magnitude when reacted with iodine (from  $10^{-4}$  S/cm to  $10^2$  S/cm).<sup>(9)</sup> This phenomenon is known as doping, and is the result of the formation of a charge carrier (Figure 1) in the polymer backbone structure. In addition, by varying the doping level, it was possible to yield polymers exhibiting a wide range of electrical properties, from insulator and semi-conductor to metal. Conducting polymers can be classed in many categories based on their functional groups and include poly-pyrrole, poly-aniline, poly-thiophene, poly-fluorene, poly-indole, poly-carbazole, poly-paraphenylene, poly-paraphenylene-vinylene and poly-acetylene.



**Figure 1.** The reaction of poly-acetylene with iodine as a doping agent <sup>(9)</sup>

Conducting polymers possess an extended pi-conjugated system made up of overlapped singly occupied p orbitals in the backbone of the polymer chain. Although conducting polymers possess a relatively important number of delocalized pi electrons, a large energy band gap exists between the valence band and the conduction band. Thus, these polymers are considered to be semi-conducting, at best. To be conducting, these polymers must be doped creating new states (donor or acceptor state), which exist within the band gap, and are energetically accessible to the pi electron. The conductivity of various doped and undoped polymers, semiconductors, and metals is given in Table 1.

**Table 1.** Conductivity of various conducting polymers, semiconductors, and metals <sup>(10)</sup>

Material	Conductivity (S/cm)
Gold, Silver, Copper	$\sim 10^6$
Doped polyacetylene	$\sim 10^5$
Doped polyphenylene	$\sim 10^3$
Doped polyfuran	$\sim 10^2$
Doped polyaniline	$\sim 10^1$
Polyazulene	$\sim 1$
Germanium	$\sim 10^{-2}$
Silicon	$\sim 10^{-6}$
Undoped polyaniline	$\sim 10^{-10}$
Glass	$\sim 10^{-10}$
Quartz	$\sim 10^{-12}$

A large number of doping methods is known to affect the conjugated polymers and includes chemical, electrochemical, photo-doping, charge-injection. The most common doping method is known as oxidative doping, and is accomplished by removing pi electrons from the conjugated pi system via either chemical or electrochemical oxidation. This method is known as p-doping and results in a positive charged backbone with counterions in close proximity. Another doping method, known as n-doping, injects electrons into the pi system, thereby increasing the number of pi electrons, and producing a negatively charged polymer.

Although oxidative doping is available to prepare polyaniline, a more common method of

producing doped polyaniline is known as acid-doping. This method is non-redox in the sense that the number of pi electrons in the backbone chain remains unchanged. As with the oxidative doping process, doped polyaniline may be produced in one step. The presence of the acid results in the protonation of nitrogen atom. Once protonated, the polymer chain becomes positively charged and is associated with counterions. The degree of protonation depends on the oxidation state of the polymer and the pH of the acid solution. The relative number of imines and amine nitrogen atoms depends on the oxidation state of the polyaniline. When being more basic, the imine sites are more readily protonated than the amine sites. Weak acid, such as acetic acid, is not strong enough to protonate the imine sites, even at relatively high acid concentration.

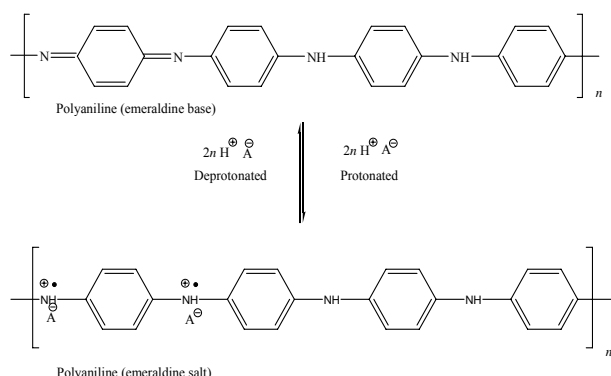
### Polyaniline

Among all conducting polymers, polyaniline (PANI) is probably one of the most intensively investigated polymers throughout the last decade. Its unique behavior includes a wide range of electrical,<sup>(11)</sup> electrochemical and optical properties,<sup>(12)</sup> as well as good stability.<sup>(13)</sup> Polyaniline can be found in three distinct oxidation states: leucoemeraldine, emeraldine and pernigraniline. Both leucoemeraldine, pernigraniline and emeraldine base show the insulating properties, but the emeraldine salt also shows the conducting properties. As for the structure, leucoemeraldine (pale brown color) with  $n=1$ ,  $m=0$  is a full reduction state. Pernigraniline (black color) is a full oxidation state,  $n=0$ ,  $m=1$ . The emeraldine ( $n,m=0.5$ ) is a half oxidation state, and this form of polyaniline is referred to as emeraldine base (blue color).<sup>(14)</sup>

The emeraldine base is regarded as the most useful form of polyaniline due to its high conductivity and stability at room temperature. In comparison the leucoemeraldine, which can be easily oxidized than the pernigraniline, is easily degraded. By considering the conductivity, emeraldine salt has the highest electrical conductivity. The basic site (imine and amine group) in the polymer backbone of the emeraldine base can be protonated with strong acid to produce emeraldine salt leading to an increase in conductivity due to the effect of charge transfer in the polymer backbone. (Figure 2). Polaron and bi-polaron are charge carriers in emeraldine salt, which move along the polymer chain upon application of electric field and are

*Interfacial Polymerization of Water-Soluble Polyaniline and Its Assembly  
Using the Layer-By-Layer Technique*

responsible for electrical conductivity. The concentration and mobility of this charge carrier determine the electrical conductivity.



**Figure 2.** Neutral and doped polyaniline<sup>(10)</sup>

Polyaniline is insoluble in water, but several methods have been developed to improve its solubility. Wei X.L. and co-workers<sup>(12)</sup> reported using sulfonic-acid self-doped polyaniline by reacting emeraldine base with fuming sulfuric acid ( $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ ) in order to promote the sulfonation of polyaniline and form SPAN. This self-doping polyaniline shows better water-solubility and thermal stability when compared with polyaniline doped with HCl. Other methods used sulfonated derivatives of aniline monomer such as *m*-aminobenzene sulfonic acid,<sup>(13)</sup> *o*-poly (3-amino-4-methoxybenzenesulfonic acid)<sup>(14)</sup> and poly (5-aminonaphthalene-2-sulfonic acid)<sup>(15)</sup> to polymerize via chemical oxidation process using ammonium persulfate as the oxidizing agent. While researchers try to develop new methods for polyaniline synthesis, recent report suggested that the interfacial polymerization of polyaniline in anionic polymeric is possible.

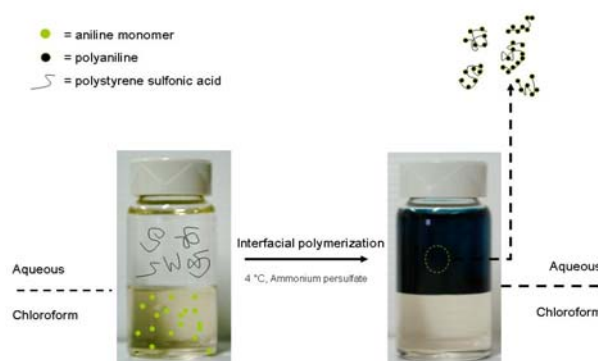
***Interfacial Polymerization (IP) of Water-Soluble Polyaniline***

Interfacial polymerization is an alternative to bulk polymerization of condensation polymers. The process requires two immiscible solvents, with monomer in one solvent reacting with the oxidant specie in the other solvent. The interfacial polymerization method provides higher molecular weights of polymer because the monomer is more likely to encounter a growing chain than the opposing monomer leading to termination of the polymerization.

Water-soluble polyaniline can be prepared via the interfacial polymerization route in the

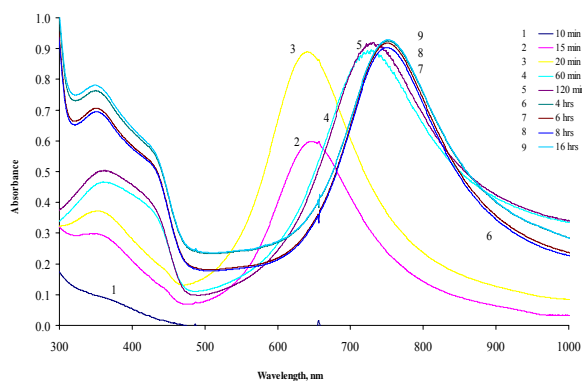
presence of PSS dispersed in the water phase. In this setup, the aniline monomers and the PSS are dissolved in  $\text{CHCl}_3$  organic phase and the aqueous phases, respectively, with the reaction taking place at the interface. Polyaniline is formed at the interface where the aniline monomer and PSS are found within 10 min in a process by which aniline is protonated by the PSS in the presence of the oxidant, ammonium persulfate. During this oxidative polymerization of aniline, the PSS acts as a proton source for the doping agent and provides the necessary counterions to the developing charged polyaniline. The excess sulfonic groups can improve water-soluble properties and the resultant polyaniline easily dispersed in aqueous solution.

Figure 3 depicts the progress of polyaniline synthesized via chemical oxidative interfacial polymerization at the bottom layer, 10 mM of aniline monomer are dissolved in  $\text{CHCl}_3$  organic solvent, and in the top layer 10 mM of PSS, which is an anionic polymer are mixed with 5 mM ammonium persulfate as the oxidizing agent. The reaction took place at 4°C without any stirring. The polyaniline was formed in the interface between organic and aqueous phase within 15 minutes and the reaction was completed within 4 hours as can be seen on the kinetic measurement shown in Figure 4. The green solution appeared in the top aqueous layer.



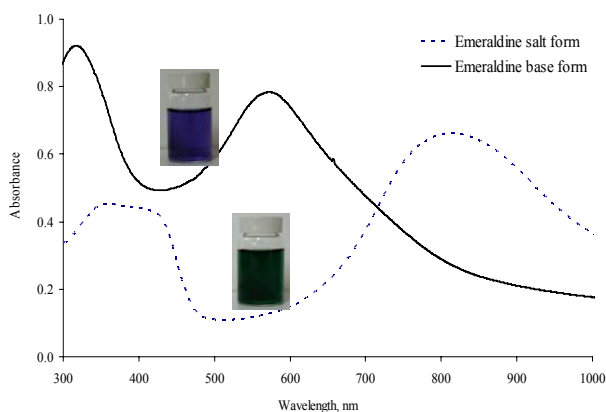
**Figure 3.** Polymerization through the  $\text{CHCl}_3$  /water interface





**Figure 4.** UV-Visible spectra and photograph of the rate polymerization of polyaniline capped polystyrene sulfonic acid

The UV-Vis spectra of polyaniline capped PSS are shown in Figures 5. Doped forms of polyaniline or emeraldine salt show three characteristic absorption bands at 350, 420 and 770 nm corresponding to  $\pi$ - $\pi^*$  band-gap absorption, low wavelength polaron- $\pi^*$  band and high wavelength  $\pi$ -polaron band, respectively. The un-doped form of polyaniline or emeraldine base shows a low wavelength  $\pi$ - $\pi^*$  band at 320 nm and a strong absorption band at 575 nm, attributed to a local charge transfer between a quinoid ring and the adjacent imine-phenyl-amine unit.<sup>(15)</sup>



**Figure 5.** UV-Visible spectra of polyaniline capped polystyrene sulfonic acid in two different forms, emeraldine base (blue form), emeraldine salt (green form)

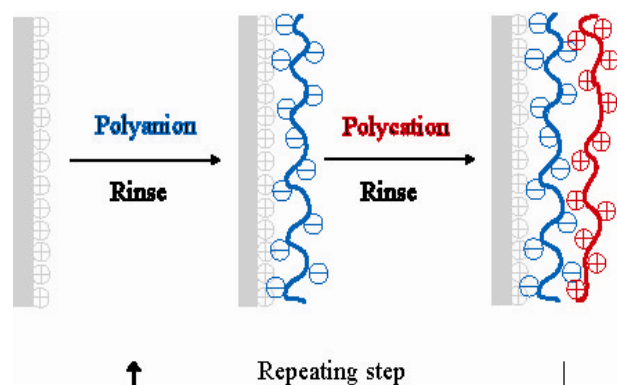
The advancement of interfacial polymerization is not limited to the synthesis of the conducting polymer, but also includes the usage of template in the aqueous layer is the interesting point for synthesis composite polymer such as zeolite, metal nanoparticles and bio-molecules, as they could change the new properties of each polymer composite materials. Feng studied the platinum nanoparticles

loaded on the aqueous layer of PSS through the interfacial polymerization of aniline.<sup>(16)</sup> They reported that the platinum nanoparticles could be prepared with polyaniline capped polystyrene sulfonic acid. They also demonstrated that the composite is obtained by incorporating Pt nanoparticles into conductive polyaniline matrix by the reduction of  $Pt^{4+}$  ions to Pt nanoparticles during the oxidative polymerization of aniline in PSS as medium.

### Polymer Nano-Thin Film

Over the last decade the development of the polyelectrolyte multilayers (PEMs) has been used for the fabrication of nanostructure films.

This increasing interest is due to the simple and reproducible method for the preparation of nano-thin films. LbL films are achieved by sequential deposition with alternating layers of positively and negatively charged polyelectrolytes on any substrate such as conducting ITO glass, silicon, metals, quartz, polymeric surface, etc.<sup>(17)</sup> Nowadays, LbL films are being developed for applications such as electrochromism,<sup>(8)</sup> catalysis,<sup>(17)</sup> electrochemical sensing<sup>(18)</sup> and biosensing and sensors.<sup>(19-21)</sup> A schematic diagram illustrating the LbL technique is shown in Figure 6. The multilayer deposition can be achieved by sequential dipping of the substrate in cationic and anionic solutions. After deposition of each layer the substrate is immersed into the washing solution and dried. The roughness, thickness and porosity of the film can be controlled at the molecular level upon adjusting experimental parameters such as pH, ionic strength and polyelectrolyte concentration.

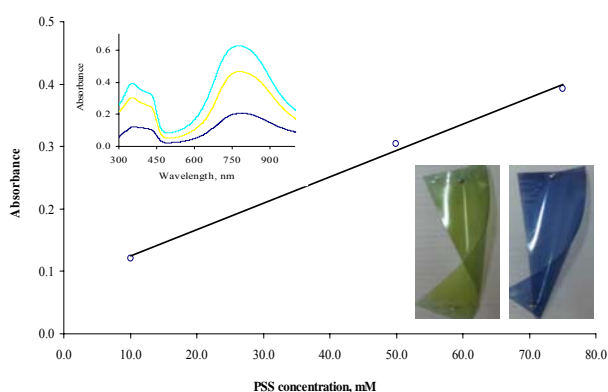


**Figure 6.** Schematic fabrication of layer-by-layer films

Conducting polymers can also be used as some of the polyelectrolytes used in the LbL assembly for fabricating nano-thin films. The resulting conducting

*Interfacial Polymerization of Water-Soluble Polyaniline and Its Assembly  
Using the Layer-By-Layer Technique*

films can be composed of conjugated polymer such as polyaniline or polypyrrol. The LbL self-assembly is probably the most versatile method for the fabrication of polyaniline nano-thin films from the water-soluble polyaniline solution since the processes do not require any organic solvent. Figure 7 shows the polyaniline films from LbL techniques by using PDAD as a polycation. It was found that when varying the PSS concentration, the absorbance of polyaniline films increases significantly due to the excess amount of PSS leading to a more anionic character of the polyaniline structure. Therefore, when building the polyaniline films with a high concentration of PSS, a high absorbance can be observed.



**Figure 7.** UV-Visible spectra of polyaniline-capped polystyrene sulfonic acid films exposed to various concentrations of PSS (10, 50 and 75 mM)

## Conclusion

Interfacial polymerization of polyaniline is a new method for synthesis of water-soluble polyaniline. The mechanism for this growth is believed to involve some alignment of the aniline monomer onto the anionic doping polymer. The in-situ polymerization technique for the preparation of water-soluble polyaniline in the presence of anionic polymeric such as polystyrene sulfonic acid allows for fabrication of the polyaniline nano-thin films. LbL self-assembly technique than can be applied to produce conducting thin films which can be used as electrode of organic displays.

## References

- Ambrosi, A., Morrin, A., Smyth, M.R. and Killard, A.J. 2008. The application of conducting polymer nanoparticle electrodes to the sensing of ascorbic acid. *Anal. Chim. Acta.* **609** : 37–43.
- Brazdziuviene, K., Jureviciute, I. and Malinauskas, A. 2007. Raman spectroelectrochemical study of polyaniline and sulfonated polyaniline in solutions of different pH. *Electrochim. Acta.* **53** : 785–791.
- Wang, Y.Y. and Jing, X.L. 2004. Preparation of an epoxy/polyaniline composite coating and its passivation effect on cold rolled steel. *Polym. J.* **36** : 374–379.
- Ghanbari, K., Mousavi, M.F. and Shamsipur, M. 2007. Synthesis of polyaniline/graphite composite as a cathode of Zn-polyaniline rechargeable battery. *J. Power. Sources.* **170** : 513–519.
- Paul, R.K., Pillai, C.K.S. and Mattes, B.R. 2000. Melt/solution processable conducting polyaniline with novel sulfonic acid dopants and its thermoplastic blends. *Synth. Met.* **114** : 27-35.
- Blinova, N.V., Stejskal, J., Trchova, M., Prokes, J. and Omastova, M. 2007. Polyaniline and polypyrrole: A comparative study of the preparation. *Eur. Polym. J.* **43** : 2331-2341.
- Nuraje, N., Su, K., Yang, N.L. and Matsui, H. 2008. Liquid/liquid interfacial polymerization to grow single crystalline nanoneedles of various conducting polymers. *ACS Nano* **2** : 502-506.
- Sarkar, N., Ram, M.K., Sarkar, A., Narizzana, R., Paddeu, S. and Nicolini, C. 2000. Nanoassemblies of sulfonated polyaniline multilayers, *Nanotechnology.* **11** : 30-36.
- Barros, R.A., Azevedo, W.M. and Aguiar, F.M. 2003. Photo-induced polymerization of polyaniline. *Mater. Charact.* **50** : 131-134.
- Lui, W., Kumar, J. and Tripathy, S. 1999. Enzymatically synthesized conducting polyaniline. *J. Am. Chem. Soc.* **121** : 71-78.
- Dong, H., Prasad, S., Nyame, V. and Jones, W. 2004. Sub-micrometer conducting polyaniline tubes prepared from polymer fiber templates. *Chem. Mater.* **16** : 371-373.

12. Wei, X.L., Wang, Y.Z., Long, S.M., Bobeczko, C. and Epsteib, A.J. 1996. Synthesis and physical properties of highly sulfonated polyaniline. *J. Am. Chem. Soc.* **118** : 2545 -2555.
13. Roy, B.C., Gupta, M.D., Bhowmik, L. and Ray, J.K. 1999. Studies on water soluble conducting polymer-Aniline initiated polymerization of m-aminobenzene sulfonic acid. *Synth. Met.* **100** : 233-236.
14. Mirmohseni, A. and Houjaghan, M.R. 2008. Synthesis and characterization of water-soluble conducting poly (3-amino-4-methoxybenzenesulfonic acid). *Mol. Cryst. Liq. Cryst.* **484** : 722-727.
15. Atkinson, S., Chan, H.S.O. and Neuendorf, A.J. 2000. Synthesis of the water-soluble, electrically conducting poly(5-aminonaphthalene-2-sulfonic acid). *Chem. Lett.* **3** : 276-277.
16. Feng, J.L., Huang, L.M. and Wen, T.C. 2007. Interfacial synthesis of platinum loaded polyaniline nanowires in poly(styrene sulfonic acid). *Mat. Lett.* **61** : 4400-4405.
17. Zhang, X.Y., Chan-Yu-King, R. and Jose, A. 2004. Nanofibers of polyaniline synthesized by interfacial polymerization. *Synth. Met.* **145** : 23-29.
18. Hopkins, A.R., Sawall, D.D., Villahermosa, R.M. and Lipeles R.A. 2004. Electrically conducting polyaniline microtube blends. *Thin. Solid. Films.* **469** : 304-308.
19. Dallas, P., Stamopoulos, D., Boukos, N., Tzitzios, V., Niarchos, D. and Petridis, D. 2007. Characterization, magnetic and transport properties of polyaniline synthesized through interfacial polymerization. *Polymers.* **48** : 3162-3169.
20. Kaner, R.B. and Huang, J. 2004. A general chemical route to polyaniline nanofibers. *J. Am. Chem. Soc.* **126** : 851-855.
21. Nohria, R., Khillan, R.K. and Su, Y. 2006. Humidity sensor based on ultrathin polyaniline film deposited using layer-by-layer nano-assembly. *Sensor Actuat. B-Chem.* **114** : 218-222.