Phenol Assisted Deaggregation of Polyaniline Chains: Simple Route to High Quality Polyaniline Film

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High conducting polyaniline films were readily prepared by in situ chemical oxidative polymerization/deposition of aniline in the presence of a very small amount of organic additive such as phenol. The conductivity of a thin (∼150 nm) polyaniline film synthesized in the presence of 0.01 wt % of phenol (**r-PANI**) is an order of magnitude higher (as well as better conducting homogeneity) than that of a film (**PANI**) obtained from the conventional method without an additive. **r-PANI** also has better adhesion and electrochemical stability/reversibility, more transparency in the visible-light region, and faster/easier doping/dedoping response compared to **PANI**. The function of phenol molecule is to avoid the formation of the inter- and/or intrachain hydrogen bonding during the growth of the polyaniline chains. The deaggregation/reducing intrachain hydrogen bonding of polyaniline chains by phenol molecules was revealed with IR, SAXS, and SEM data. All these data supported that phenol does assist the deaggregation of polyaniline chains during the growth of polymer chains or nanorods.

Introduction

Polyaniline family (PANI) has been the subject of wide investigation because of its diversity in the structure, optical, electrochemical, and electrical properties as well as applications.[1] Many physicochemical properties of PANI largely depend on the structure of the polymeric backbone and the packing of the polymer chains.[2] The magnetic, optical,[3] and C-AFM data[4] had shown a phase segregation between highly conducting regions and the insulating background in a single PANI film, and the charge conduction was proposed via charging energy-limited tunneling among the small granular polymeric grains.[5] Therefore, Ginder[6] et al. believed that the conductivity of the conducting island in PANI could be up to 10^3 S/cm. Furthermore, several reports had demonstrated that the conductivity of PANI was affected by the chain length,[7] morphology,[8] texture,[9] and degree of crystallization[10] of the polymer films. A lot of approaches were used to adjust the structure/conformation of polyaniline chains to further increase the conductivity of the polymer film. One of the most estimable methods was demonstrated by MacDiarmid et al., who used a strategy called "secondary doping".[11] The secondary dopant is an inert solvent, and its function is to solvate the counteranions of the polymers, increase the repulsion between positively charged polymer backbones, decrease the aggregation, and, therefore, increase the crystallinity and conductivity of the polymer films.

Inspired by the concept of secondary doping, in this article, we reported a very simple route to decrease the aggregation of the polyaniline chains to increase the conductivity of PANI films. Instead of treating the polyaniline with the vapor of organic solvent (secondary dopant) after the film was fabricated as the procedure for the secondary doping, we added a very small amount of functional additive, such as phenol, in the reaction media during the process of the polymerization/

deposition of polyaniline films on ITO substrate. The charge transport and physicochemical properties of polyaniline films on ITO substrates prepared with/without phenol molecules were investigated, and the function of phenol additive during the chemical polymerization of aniline was discussed.

Experimental Section

Chemicals. Water was purified using a Milli-Q (Millipore Corp., Bedford, MA) purification system with a resistivity of 18 MΩ cm. ITO substrate (Merck Display Technologies Ltd., with ITO thickness of 100 nm and surface resistance of ∼ 20Ω/square) was cut into 20 × 20 mm. Silicon wafer ((100) oriented, p-type) was obtained from Topsil Co. Aniline (ACROS, ACS grade) was used after distilling over calcium hydride and stored in the dark under a nitrogen atmosphere. $HCl_{(aq)}$, 0.1 M $NH_4OH_{(aq)}$, phenol, and $(NH_4)_2S_2O_8$ were obtained from commercial resources and used without further purification.

Preparation of PANI Films and Powders. Polyaniline films on ITO substrates were prepared by in situ polymerization/deposition of aniline as reported in the literature,[12] except the polymerization was carried out at room temperature without mechanical agitation. Aniline (0.17 g, 1.8 mmol) and $(NH_4)_2S_2O_8$ (0.41 g, 1.8 mmol) were well-dissolved in 26 and 10 mL of 1.2 M $HCl_{(aq)}$, respectively. The ITO substrates were put at the bottom of the reaction box (with the ITO face up) before aniline/$HCl_{(aq)}$ and $(NH_4)_2S_2O_8$/$HCl_{(aq)}$ were added into the reaction box. Polyaniline film grew automatically on the ITO substrate. Prior to the analysis, the as-prepared polyaniline film was first dipped in 0.1 M $NH_4OH_{(aq)}$ for 2 min (to ensure that it is fully dedoped to emeraldine base (EB)), washed with distilled water, and dried under a stream of N_2 gas. The doping (protonation) process was carried out by dipping the EB films into 0.1 M $HCl_{(aq)}$ solution, and the UV/vis/NIR spectra were used to monitor the doping levels of PANI films. Upon dipping in acid, EB converts to emeraldine salt (ES) and the λ_{max} shifts to longer wavelength. When the λ_{max} of ES stopped to red-shift, it is an indication that the PANI films are fully doped/protonated. Polyaniline films on Si substrate was prepared under

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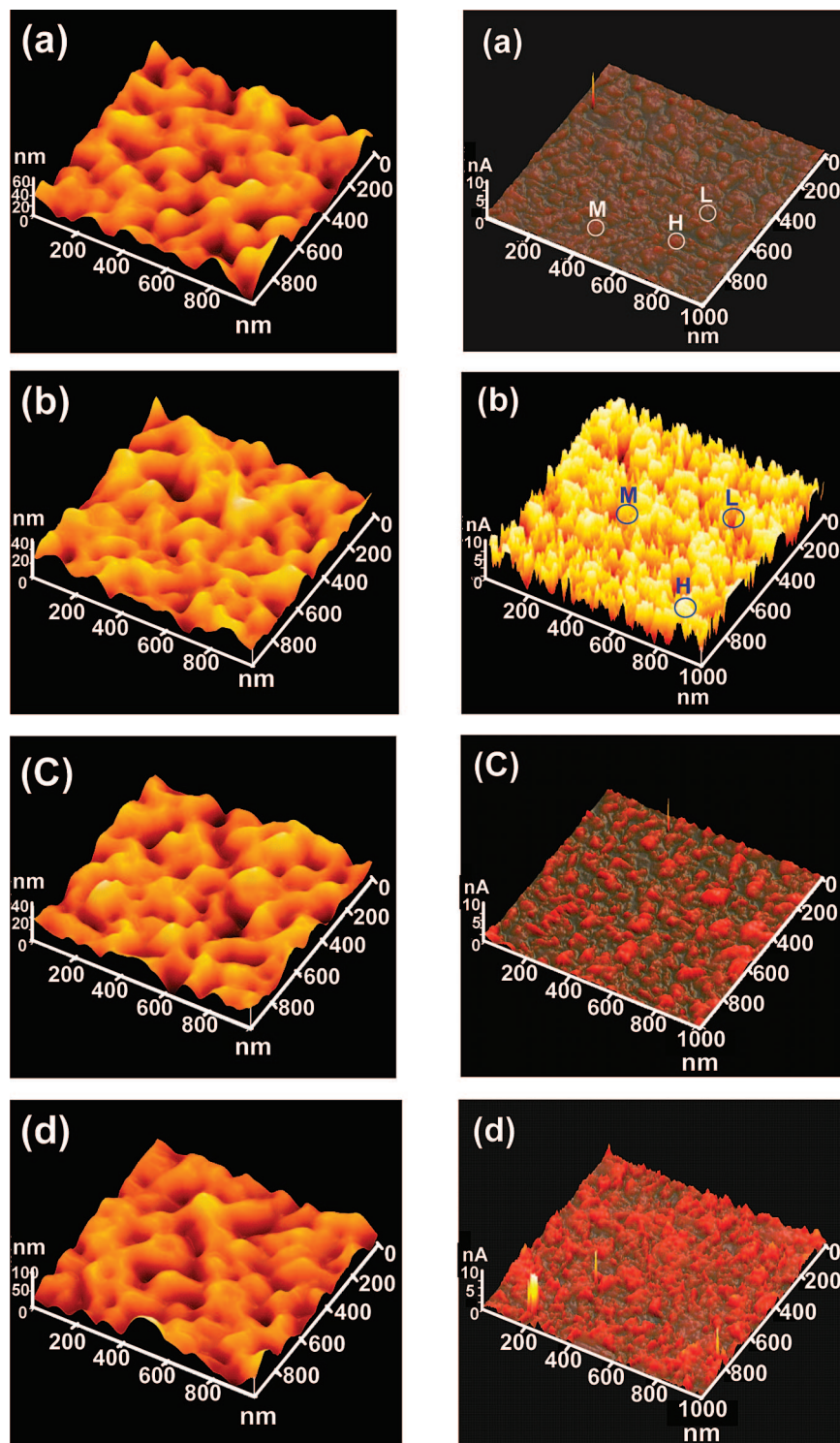*J. Phys. Chem. B, Vol. 112, No. 22, 2008* **6773**

Figure 1. The AFM (left) and C-AFM (right, applied voltage = 3mV) diagrams of polyaniline films prepared in the presence (a) none, (b) phenol, (c) toluene, and (d) methanol.

the same conditions as those using ITO as a substrate.[13] During the deposition of polyaniline film, some powders were formed in the reaction solution. The powder was isolated by filtration, washed with acidic solution and then distilled water, and dried in air. The procedures for preparing polyaniline film and powder in the presence of organic additive are similar to the steps described above, except certain amount of organic additive was mixed with aniline/HCl$_{(aq)}$ before contacting with $(NH_4)_2S_2O_8$/HCl$_{(aq)}$. The mole ratio of phenol to aniline used in this study varied from 0.0001 to 0.1, and the mole ratio for the rest additives is 0.0001. The film thickness was determined by a

Veeco Instruments Dektak3 surface profile meter and by the absorption intensity at 600 nm. The calibration curve of absorption intensity vs film thickness was obtained by measuring the absorbance at 600 nm as well as by measuring the thickness (SEM images of the film cross-section) of the polyaniline films. The rate of film growth is affected by the concentration of the additive, and therefore different deposition times were used to prepare polyaniline films with a similar thickness.

C-AFM Studies. Samples for conducting atomic force microscope (C-AFM) study were mounted, using silver paste, to the AFM sample holder. The contact mode AFM with a

TABLE 1: The AFM and C-AFM Data of Polyaniline Films Prepared at Various Reaction Conditions

additive	none	phenol	toulene	methanol
film thickness (nm)	150	154	150	152
rms[a] (nm)	14.3	12.1	11.9	22.6
applied voltage (mV)	3	3	3	3
average current[b] (nA)	0.43	6.57	0.55	1.17
conducting homogeneity[c]	0.47	0.34	0.78	0.67
average conductivity[d] (S/cm)	0.06	0.66	0.07	0.14

[a] Root-mean square of the surface roughness. [b] The average of the current within the measured area (32768 data points in the area of 1 $\mu m \times 1 \mu m$). [c] Conducting homogeneity is equal to I_{rms}/I_{avg}, where I_{rms} is a root-mean square of the current ($I_{rms} = \sqrt{\Sigma(I_i - I_{avg})^2/n}$). The smaller value indicated better conducting homogeneity. [d] We measure 10 areas in each film. The data are the average of the 10 measurements, and some C-AFM images and $I-V$ curves are not shown in this article.

TABLE 2: The GPC Data of Polyaniline Film and Powder

sample	LiCl	M_w	PDI
r-PANI film	no	17 600	1.2
	yes	12 800	1.3
PANI film	no	18 400	1.2
	yes	11 800	1.3
r-PANI powder	no	18 000	1.2
	yes	13 500	1.4
PANI powder	no	20 000	1.2
	yes	15 800	1.4

current-sensing module (SPA400, SEIKO Inc., Japan) was used to simultaneously measure the topographical and current images. The detailed experimental procedures and data analysis can be found in the previous articles.[4]

Physicochemical Measurements. UV−Vis−NIR spectra were obtained using Varian Cary 5E spectrophotometer in the laboratory atmosphere at room temperature. Fourier transform infrared (FTIR) spectra were recorded for polyaniline film on Si substrate using a Bio-Rad 155 FTIR spectrometer at ambient temperature with a resolution of 4 cm^{-1}. Scanning electron micrograph (SEM) was recorded with a Hitachi S-800 at 15 KV. The samples (film on ITO glass or powder) for SEM imaging were mounted on metal stubs with a piece of conducting tape and then coated with a thin layer of gold film to avoid charging. Electrochemistry of the polymer films was performed in a single-compartment, three-electrode cell with a polyaniline coated ITO working electrode and a Pt coil counter electrode. The reference electrode was Ag/AgNO$_3$ and the supporting electrolyte was 0.1 M HClO$_{4(aq)}$. The cyclic voltammograms were recorded using an Autolab system (PGSTAT 30, Autolab, Eco-Chemie, Netherland). The weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters-2487 instrument using NMP as an eluent and polystyrenes as standards. Small angle X-ray scattering was measured with the instrument installed at the wiggler beamline BL17B3 of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. This instrument is designed for studies of static and dynamic nanostructures, provides a flux of 10^{10}−10^{11} photon s^{-1} at the sample at energies between 5 and 14 KeV. A SAXS area detector operated in master-slave mode was used for recording the signal. Data reduction algorithms have been developed for rapid processing of the large data sets. The scattering data of polyaniline film on ITO substrate were obtained by subtracting the background scattering from the ITO substrate.

Results and Discussion

The Reaction Conditions for Preparing High Conducting Polyaniline Films. Polyaniline films on ITO substrates studied in this article were prepared by the in situ polymerization/deposition method as reported previously[12] except that the polymerization was carried out at room temperature without mechanical agitation. Furthermore, various types of additive, such as phenol, *p*-aminophenol, *m*-aminophenol, nitrobenzene, toluene, hexane, or methanol were well-mixed with aniline (in 1.2 M HCl$_{(aq)}$) before contacting with the oxidant solution. The typical mole ratios for additive to aniline are 1:10 000 (0.01%). It was found that all the additives slow down the film deposition rate. For instance, it takes 9 and 8 min, respectively, to grow 150 nm polyaniline films with (0.01%) and without phenol additive. Therefore, different deposition times were used to control the film thickness. To exclude the effect of film thickness on the properties of polymer, the thickness of polyaniline films was maintained as close as possible.

The Effect of Additives on the Charge Ttransport Properties of the in Situ Polymerized/Deposited Polyaniline Film. Figure 1 shows the typical topographic (left) and current (right) images obtained simultaneously for an identical part of the polyaniline films prepared in the presence of various additives, and the related data are summarized in Table 1. The globular-shaped image which is a typical topography for polyaniline films prepared from HCl$_{(aq)}$[14] was observed. The morphology observed in the topographic images is similar but the conductivity is different for polyaniline films prepared with and without an additive (see Figure 1). Polyaniline film prepared in the presence of phenol has a higher conductivity and better conducting homogeneity (see Table 1). The average conductivity of polyaniline thin film (∼150 nm) prepared in the presence of 0.01% phenol (**r-PANI**) is an order of magnitude higher than that of the film (**PANI**) prepared with a conventional method (without additive). The addition of methanol also increased the conductivity of polyaniline film. Nevertheless, the conducting homogeneity decreased. On the other hand, some additives, such as hexane and toluene does not affect the conductivity of polyaniline films. As seen in Table 1, the addition of phenol has the highest impact on the charge transport properties of polyaniline films among the additives used in this study. Therefore, the following discussion was focused on the effects of the phenol additive. Figure 2 showed the $I-V$ curves of the selected areas (shown in right side of panels a and b of Figure 1, respectively) for **r-PANI** and **PANI** films. The conducting characteristics[15] of the polyaniline films were evolved with the same method reported previously.[4] Inspection of the $I-V$ curves at different spots of **r-PANI** film reveals that the local conductivity of the polymer film is very homogeneous. Only metallic conducting behavior was detected at the three (the high and low conducting areas and one in-between) selective conducting areas. Nevertheless, the $I-V$ curve corresponding to semiconductor-like conducting behavior was observed at the low conducting region of **PANI** film. The conductivity, σ, within each region was estimated from the $I-V$ curves using eq 1 and assuming a contact radius between C-AFM tip and polymer film of 50 nm.[15]

$$\sigma = d/(A_t R) \tag{1}$$

In the above equation σ is the conductivity, d is the film thickness, A_t is the area of the C-AFM probe in contact with the surface, and R is the resistance of the sample, estimated from the inverse slope of the $I-V$ curve. When the $I-V$ curve is not linear, the slope of the curve was estimated from the linear fit of the curve.
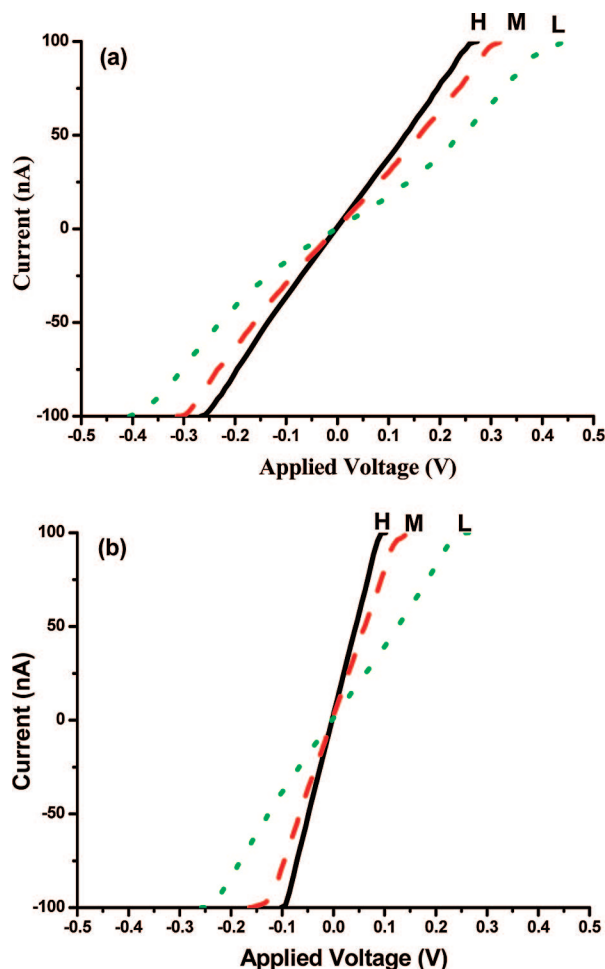
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Figure 2. The three *I*−*V* curves of the selected areas for (a) **PANI** (right diagram of Figure 1a) and (b) **r-PANI** (right diagram of Figure 1b) films.

Figure 3. (a) The UV/vis/NIR spectra of doped (a) **PANI** and **r-PANI** films (film thickness = 161 nm). (b) Average transmittance (at the region of 400−800 nm) vs film thickness of **PANI** and **r-PANI** films.

By use of this approximation, the conductivities of the ten conductive regions were calculated, and the average values are listed in Table 1. The conducting inhomogeneity of polyaniline film is perhaps due to the fact that polyaniline chains in some regions are more aggregated and, thus, less conductive than other regions. The C-AFM data can not provide directly the assessment of the difference in the chemical identity between high and low conductive regions. However, the high conducting regions likely corresponds to better ordered, less aggregated polyaniline chains, previously identified by the spectroscopic methods.[16] In consequence, we can assume that less aggregated polyanilne chains were formed when the polymerization/ deposition was carried out in the presence of phenol molecules.

Polyaniline film prepared in the presence of phenol has not only higher conductivity but also better adhesion and electrochemical stability/ reversibility, more transparency in the visible range, and faster/easier doping/dedoping response toward acid/ base (vide infra) compared to those obtained without phenol additive. The introduction of phenol additive in the polymerization media was proved to be a very facile and effective way to improve the conductivity and properties of polyaniline films.

The Effect of Phenol Molecule on the Transparence, Adhesion, and Chemical/Electrochemical Reversibility of the in Situ Polymerized/Deposited Polyaniline Film. The UV−Vis−NIR spectra of doped **r-PANI** and **PANI** films (at the thickness of ∼150 nm) are displayed in Figure 3a. It was found that all the three absorption peaks of **r-PANI** are red-shifted compared
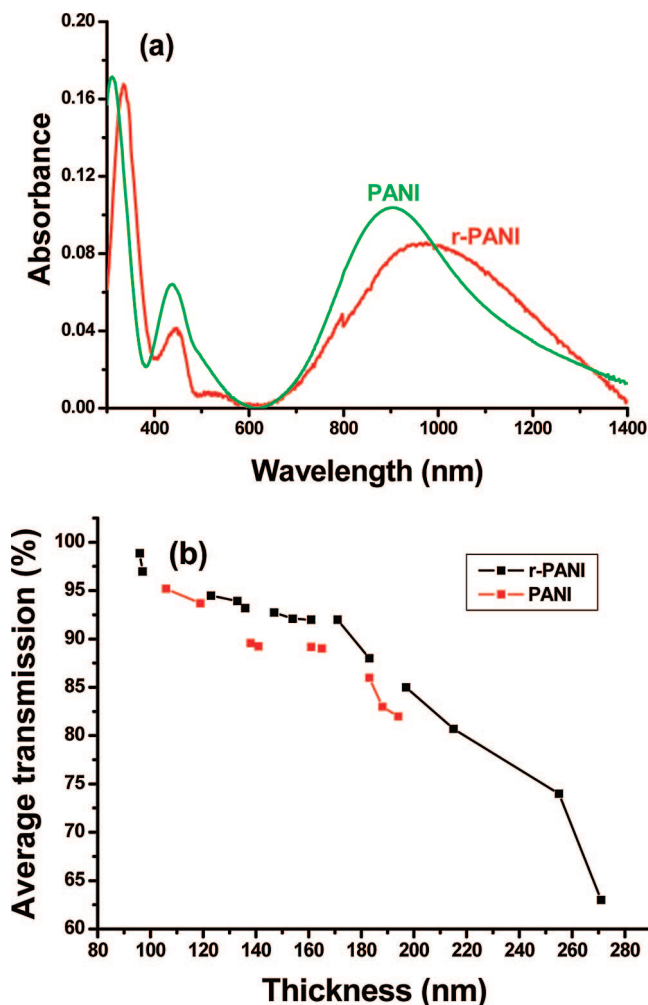
to those of **PANI** film. Furthermore, the intensity of the peak centered at 430 nm, which is assigned to the polaron to π^* transition,[17] decreased significantly. The decrease in the intensity of the peak at ∼430 nm and the red-shift of the polaron peak (the lowest energy peak) makes the film more transparence in the visible light region. We do not know exactly why the intensity of the peak at 430 nm decreased. Nevertheless, the red-shift of the polraon peak of **r-PANI** suggested that the polymer chains in **r-PANI** film existed as a more expanded coil-like conformation. For more quantitative comparison, the thickness dependent average transmission (from 400 to 800 nm) of **r-PANI** and **PANI** films at various thicknesses was plotted in Figure 3b. It was clearly seen in Figure 3 that for the similar thickness, **r-PANI** has higher transparence at the visible-light zone compared to that of **PANI**. The higher conductivity and more transparence in the visible region of **r-PANI** film were attributed to the more expanded coil-like conformation (less intrachain hydrogen bonding) of polyaniline chains formed in the presence of phenol additive. Moreover, the adhesion of **r-PANI** film is also better than that **of PANI** film; **r-PANI** film sticks well on ITO substrate at the film thickness higher than 250 nm, nevertheless, when the **PANI** is thicker than 200 nm, part of the film will come off the ITO substrate. The conformation of the polymer chains affects not only the conductivity and transparence but also the chemical and electrochemical properties of the polymer films. For example, **r-PANI** film can be fully doped with 10^{-2} M $HCl_{(aq)}$.
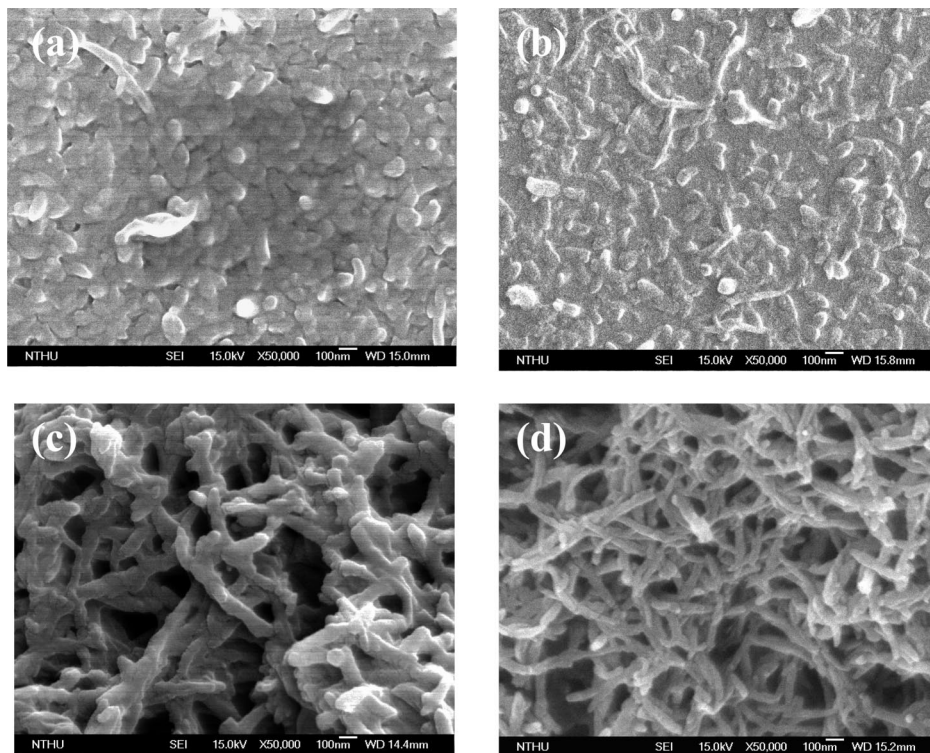
Figure 4. SEM micrographs of (a,c) **PANI** film and polyaniline powder obtained from the solution without additive and (b,d) **r-PANI** film and polyaniline powder obtained from the solution with phenol additive.

On the other hand, to fully dope **PANI** film, the concentration of $HCl_{(aq)}$ should be higher than 10^{-1} M. **r-PANI** also has lower red-ox potentials and better electrochemical reversibility; The red-ox potentials are 0.5 V/−0.4 V and 0.6 V/−0.6 V (vs Ag/AgCl) for **r-PANI** and **PANI**, respectively.

The Function of Pphenol Additive during the Aniline Polymerization Process. It will be a great value to know about the function of phenol molecule in the process of the chemical oxidation polymerization of aniline. The polymerization of aniline is an exothermic process and it has long been recommended to be carried out at low temperatures under vigorous stirring.[18] The resulting polymer powder has an aggregated granular morphology.[15] It seems that the aggregation, during chemical oxidation, nucleation, chain growth, and precipitation, of polyaniline chains is caused by the agitation or fast reaction of aniline oligomers, since more hydrogen bonding can be formed when polymer chains have more chance to contact with each other or bend (folded back) themselves. This is probably also the reason that loose nanorod or nanofiber can be obtained when the chemical polymerization was performed at room temperature or without stirring[19] or interfacially.[20] Then, what is the function of additive such as phenol molecule in the polyaniline chain growth and film formation process?

We found that the initial polymerization time (the time need to observe the formation of the blue-green fiber in the solution after the aniline and oxidant were mixed) is longer, and the polymerization releases less heat when the phenol molecule was added into the reaction solution. Phenol molecules also affect the film growth rate; the higher phenol concentration, the slower is film growth speed. These phenomena seem to indicate that phenol molecules are involved in the chain growth process of polyaniline. Phenol reduces the rate of polymerization by breaking the intra- and interchain hydrogen bonding during the growth of polyaniline chains. In order to further address the aggregation of the polyaniline chains, the molecular weight of

both powder and film (prepared with or without phenol additive) were also measured in the presence of LiCl, and the data are listed in Table 2. GPC data showed that the molecular weight of polyaniline measured from LiCl/NMP solution is lower than that measured from pure NMP solution. LiCl was known as a salt to deaggregate the polyaniline chain. GPC data revealed that, compared to **r-PANI**, **PANI** deaggregated more in the presence of LiCl, suggesting that **PANI** chains are more aggregated. Although the aggregation of the polyaniline chains can not be observed directly from the SEM micrographs of **r-PANI** and **PANI** films, we found that thinner and longer polyaniline nanorod powder was obtained when the polymerization was carried out in the presence of phenol (see Figure 4). When the polymer chains were less aggregated they could grow longer before precipitating from the solution. Therefore, if the intrachain hydrogen bonding was reduced, thinner and longer (more homogeneous in size) nanorods (or fibers) will be formed. However, the length of the polyaniline nanorod observed in the SEM micrographs is not consistent with the chain length calculated from the GPC data. For example, based on the GPC data, polyaniline chain prepared in the presence of 0.01 mol % phenol contains 204 aniline units, which is ca. 100 nm in length. Nevertheless, SEM revealed that the nanorod is ca. 50 nm in diameter and the length is much longer than 100 nm. These results suggested that the mechanism for the formation of polyaniline nanorods is a very complicated. It may involve the intra- and interchain interactions: mainly hydrogen bonding or may be $\pi-\pi$ interaction. If these chemical interactions were interrupted during the chain growing process, then polyaniline chains and therefore polyaniline with varied physical/chemical properties can be prepared.

To further address the presence of the hydrogen bonding, polyaniline films deposited on Si wafers were prepared and the IR spectra were taken (as shown in Figure 5). It was found that the intensity of the absorption peaks at ~3297 and ~3391 cm^{-1},

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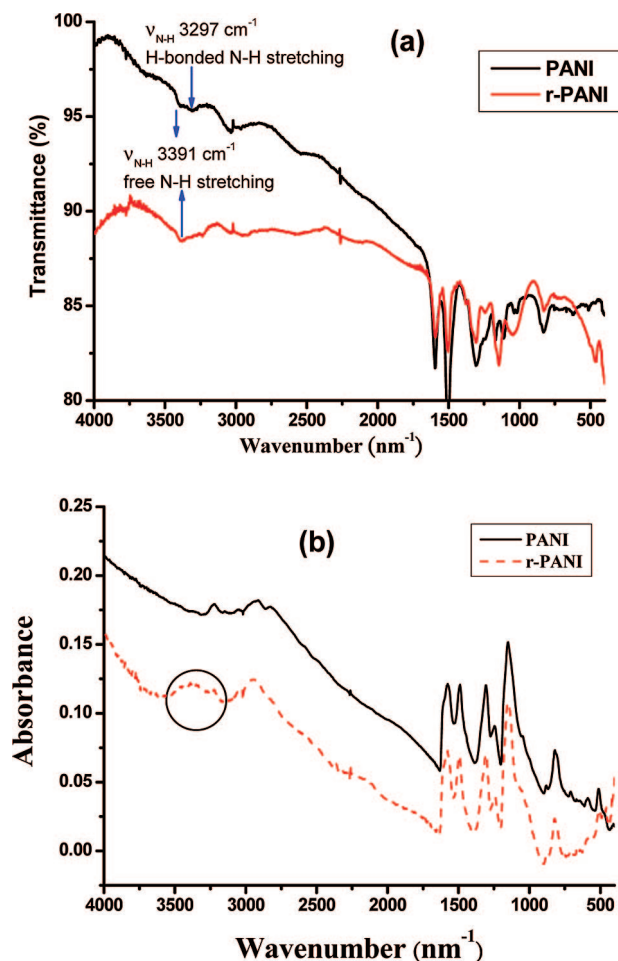*J. Phys. Chem. B, Vol. 112, No. 22, 2008* **6777**

Figure 5. The IR spectra of (a) EB form of **PANI** and **r-PANI** and (b) ES form of **PANI** and **r-PANI** films on silicon substrates.

which have been assigned to the H-bonded N−H stretching and free N−H bond, respectively,[21] are similar for **PANI** (EB) film. On the other hand, the absorption peak at ∼3391 cm^{-1} is strong but the peak at ∼3297 cm^{-1} is rather weak for **r-PANI** (EB) film. The result suggested that more hydrogen bonded N−H groups were present in **PANI** film. Furthermore, the absorption at ∼3391 cm^{-1} (the free N−H bond) of **r-PANI** (ES) film is very broad and much stronger than that of **PANI** (ES) after being doped (see Figure 5b), indicating that **r-PANI** film has a higher degree of protonation when it is doped with acid. Although a quantitative determination of the degree of hydrogen bonding cannot be made only by the IR data, the IR data do support that polyaniline chains with less hydrogen bonding are formed when the polymerization is carried out in the presence of phenol additive, although we do not know whether the reduction in the hydrogen bonding by phenol molecules occurs during the polymer chain growing process or the nanorod formation process. Surprisingly, the phenol assisted deaggregation of polyaniline chains happened at a phenol to aniline mole ratio as low as 0.01%. However, when the concentration of phenol in the reaction mixture is higher than 10%, no conductivity enhancement was found. When the amount of phenol is up to 100%, the polymerization became very slow; almost no polyaniline film was formed on the ITO substrate.

In order to directly explore the conformation or ordering of polyaniline chains of the films on ITO substrates, small-angle X-ray scattering (SAXS) measurements using a synchrotron radiation source were performed, and the results are displayed in Figure 6. The radius of gyration (*R*g) of the particles in
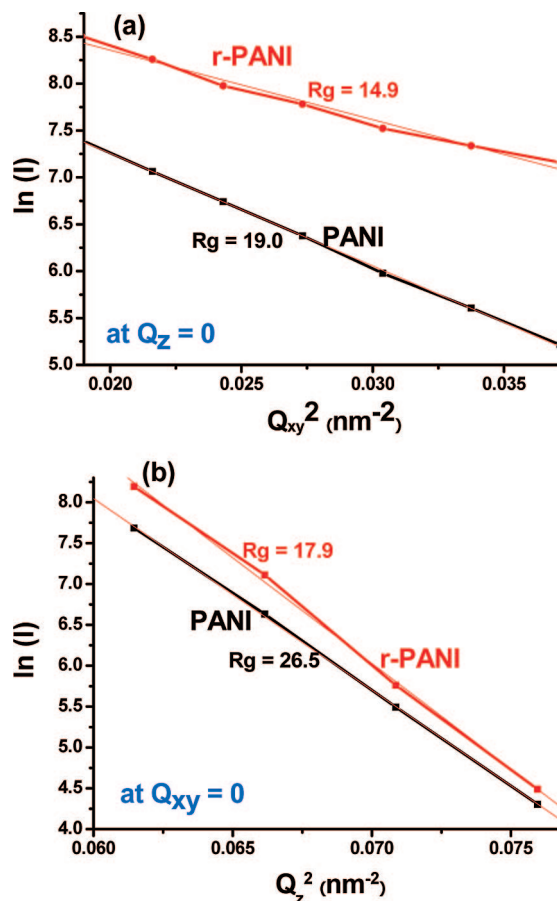

Figure 6. Guinier plots (ln $I(q)$ vs q^2) of the SAXS patterns for **PANI** and **r-PANI** films (a) on XY plane and (b) on Z direction.

polyaniline films was evaluated with the Guinier theory[22] at low angles using the equations shown below:

$$I(q) = I(0)\exp\left(\frac{-Rg^2}{3}q^2\right) \tag{2}$$

$$\ln[I(q)] = A + B(q^2), \ B = \frac{-Rg^2}{3} \tag{3}$$

The Rg values obtained from the slope of the ln[$I(q)$] vs q^2 curves at both *xy* plane and *z* axis direction suggested that longer and thinner polyaniline rods were formed when the polymerization was carried out in the presence of phenol (although the exact *R*g values are not calibrated in this study). The results are similar to what was observed on polyaniline powder isolated from the polymerization solution (see Figure 4).

Conclusion

We discovered a very simple method to enhance the quality of polyaniline thin films by adding an additive, such as phenol, in the reaction medium during the polymerization/deposition process. The specific interactions involving hydrogen bonding and π−π interaction between phenol and aniline oligomer or polymer during the growth of the polymer chains were proposed. These specific interactions may be critically important for the conformation of the polyaniline chains and therefore the conductivity and physicochemical properties of the resulting polymer film. The alignment of polyaniline chains to achieve higher conductivity has been pursued in the conjugated polymer community for many years. We found a very simple and reproducible way to straighten the polyaniline chains. Moreover,

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in the application of plastic electrode on the flexible electronic devices, there is a challenge to increase the conductivity of polymer to match the existing conventional materials. The fabrication of high conducting polymer thin films in a simple and reproducible way makes the development of plastic electrode a step closer to reality.

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