Enzymatically Synthesized Conducting Polyaniline

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Abstract: A novel strategy for the enzymatic synthesis of a water-soluble, conducting polyaniline (PANI)/sulfonated polystyrene (SPS) complex is presented. The enzyme horseradish peroxidase (HRP) is used to polymerize aniline in the presence of a polyanionic template, sulfonated polystyrene. The synthesis is simple, and the conditions are mild in that the polymerization may be carried out in a 4.3 pH buffered aqueous solution, with a stoichiometric amount of hydrogen peroxide and a catalytic amount of enzyme. UV−visible absorption, FTIR, GPC, elemental analysis, and conductivity measurements all confirm that the electroactive form of PANI, similar to that which is traditionally chemically synthesized, is formed and complexed to the SPS. The reversible redox activity of the polyaniline displays a unique hysteresis loop with pH change. Cyclic voltammetry studies show only one set of redox peaks over the potential range of −0.2 to 1.2V, which suggests that the PANI/SPS complex is oxidatively more stable. The conductivity of the complex is found to increase with the molar ratio of PANI to SPS. Conductivities of 0.005 S/cm are obtained with the pure complex and may be increased to 0.15 S/cm after additional doping by exposure to HCl vapor. This enzymatic approach offers unsurpassed ease of synthesis, processability, stability (electrical and chemical), and environmental compatibility.

Introduction

In recent years there has been a tremendous interest in the use of conducting polymers in electronics applications because of their wide range of electrical, electrochemical, and optical properties as well as their good stability.[1−3] In particular, polyaniline (PANI) has been investigated for such applications as organic lightweight batteries,[4] microelectronics,[5] optical displays,[6] antistatic coatings, and electromagnetic shielding materials.[7] PANI is commonly synthesized by oxidizing aniline monomer either electrochemically or chemically.[8,9] The final electroactive polymer can exist in various oxidation states, which are characterized by the ratio of amine to imine nitrogen atoms.[10] PANI can be doped either by protonation with a protonic acid or by charge-transfer with an oxidation agent,[11] and the electronic and optical properties may be controlled reversibly by varying the doping level.[11b, 12]

For practical applications, a conducting polymer must be cost-effective to synthesize and purify, have good chemical and electrical stability, and be able to be easily processed from either solution or the melt.[13] PANI, although one of the most promising conducting polymers from the standpoint of application, has nevertheless found only limited commercial application due to harsh or limited chemical synthetic procedures and poor solubility in common solvents. Many attempts have been made to improve the processability of PANI including modification of the polymer with various ring or *N*-substitutes,[14−17] post-

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treatment of the polymer with fuming sulfuric acid, and self-doped methods.[18,19]Although these methods have demonstrated improved solubility and processability, they remain limited in the harsh synthetic conditions and involved separation and purification techniques.

Horseradish peroxidase is able to catalyze the oxidation of a wide range of compounds including aromatic amines and phenols in the presence of hydrogen peroxide to generate corresponding free radicals. In general, the catalytic cycle can be schematically written as follows:[20]

$$\mathrm{HRP} + \mathrm{H_2O_2} \rightarrow \mathrm{HRP\ I}$$

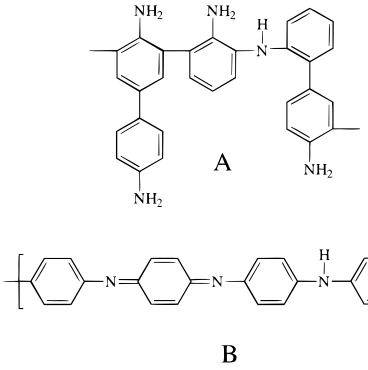
$$\mathrm{HRP\ I} + \mathrm{RH} \rightarrow \mathrm{R^*} + \mathrm{HRP\ II}$$

$$\mathrm{HRP\ II} + \mathrm{RH} \rightarrow \mathrm{R^*} + \mathrm{HRP}$$

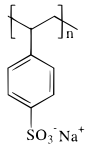
Here the native enzyme (HRP) receives 2 oxidizing equiv from hydrogen peroxide to form an intermediate HRP I. HRP I in turn oxidizes the substrate (RH) by carrying out two sequential one electron-reduction steps through a partially oxidized intermediate HRP II to return back to its original native form and repeat the process again. The substrate in this case (RH) is either a phenol or aromatic amine monomer. R* is the radical species formed of either phenol or aromatic amine. These free radicals then undergo coupling to produce the dimer, and successive oxidation and coupling reactions eventually result in the formation of polymer.[21] Recently, the use of enzymes as chemical catalysts in the synthesis of polyphenols and polyanilines has attracted great interest.[22] The enzymatic approach is environmentally benign, can offer a higher degree of control over the kinetics of the reaction, and has the potential of producing product in high yield.

A major drawback of enzymatic polymerization, however, has been that, as soon as polymer begins to form in aqueous solutions, it precipitates out and only very low molecular weight polymers (oligomers) are formed.[23] To address this and improve processability, a variety of modified enzymatic polymerizations have been investigated including solvent mixtures,[24] modified monomers in aqueous solutions,[25] micelles,[26] reverse micelles,[27] and polymerizations at the air−water interface.[28] It was found, however, that, although these polymers are of higher molecular weight, they are typically a mixture of at least two structurally different types of PANIs, as shown in Scheme 1.[24b,c] The first is that of ortho- and para-substituted carbon−carbon and carbon−nitrogen bond structures and the second is that of a benzenoid−quinoid (head-to-tail reaction), which is the desired structure formed in the traditional chemical polymerization of aniline. The presence of these highly branched ortho- and para-substituted PANIs severely limits the degree of conjugation and hence the electrical and optical properties of the resulting polymers. Therefore, although dramatic improvements have been made regarding the molecular weight, organization, and processing of these polymers, the bulk electrical and optical properties of enzymatically synthesized polymers are still not sufficient for commercial applications.

Scheme 1



Scheme 2



In the present work, a unique enzymatic approach has been developed which addresses and resolves current limitations of both enzymatic and chemical polymerization of aniline. This process inherently minimizes the parasitic branching and promotes a more para-directed, head-to-tail polymerization of aniline. This process is also simple (one-step), is environmentally benign, and results in a water soluble, high molecular weight polyaniline complex. In this approach aniline is enzymatically polymerized in the presence of a polyelectrolyte template.[29] The intent was to first electrostatically complex the aniline monomer to a polyelectrolyte template and then initiate the enzymatic polymerization. Here the polyelectrolyte would serve three critical functions. First, to preferentially align the aniline monomers and promote a more ordered para-directed reaction, second, to provide counterions for doping of the synthesized polyaniline and third, to maintain water solubility for processing. Since aniline has a known pK_a of 4.63,[30] it was expected to be primarily positively charged at pHs lower than 4.63. Sulfonated polystyrene (SPS), whose structure is given in Scheme 2, was chosen as the template in this study because of its commercial

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availability, high degree of sulfonation, and low pK_a (benzenesulfonic group has a pK_a of 0.70).[30] Thus it was expected that a pH of 4.3−4.5 would be sufficient to provide the necessary cationic and anionic charges necessary for preferential monomer alignment and salt formation with the SPS polyelectrolyte template.

This paper will discuss the enzymatic polymerization of aniline in the presence of the anionic polyelectrolyte, SPS. The reaction was carried out in mild, aqueous, pH 4.3 buffered solution. The final product is a water-soluble, electroactive, and conducting PANI/SPS complex. All characterization of this enzymatically prepared PANI is consistent with polyaniline that is traditionally prepared via either chemical or electrochemical procedures. Detailed synthesis and characterization of this simple, inexpensive, and environmentally benign synthesis of a stable and processable conducting polymer is presented.

Experimental Section

Materials. Horseradish peroxidase (EC 1.11.1.7) (200 U s/mg) was purchased from Sigma Chemical Co., St. Louis, MO, with RZ > 2.2. A stock solution of 10 mg/ml in pH 6.0, 0.1 M phosphate buffer was prepared. The activity of HRP was determined according to the Sigma method using pyrogallol as a substrate by monitoring the increase of absorbance at 420 nm in the first 20 s. Aniline (purity 99.5%) and poly (sodium 4-styrenesulfonate) (MW of 70 000 and 1 000 000) were obtained from Aldrich Chemical Co. Inc., Milwaukee, WI, and used as received. All other chemicals and solvents used were also commercially available, of analytical grade or better, and used as received.

Polymerization. The enzymatic polymerization of aniline was typically carried out at room temperature in a 30 mL, 0.1 M sodium phosphate buffer solution of pH 4.3 which contained a 1:1 molar ratio of SPS (70 000) to aniline, (6 mM) SPS (based on the monomer repeat unit) and 6 mM aniline. SPS was added first to the buffered solution, followed by addition of the aniline with constant stirring. To the solution, 0.2 mL of HRP stock solution (10 mg/ml) was then added. The reaction was initiated by the addition of a stoichiometric amount of H_2O_2 under vigorous stirring. To avoid the inhibition of HRP due to excess H_2O_2,[24a] diluted H_2O_2 (0.02 M) was added dropwise, incrementally, over 1.5 h. After the addition of H_2O_2, the reaction was left stirring for at least 1 h, and then the final solution was dialyzed (cutoff molecular weight of 2000) against pH 4.3 deionized water overnight to remove any unreacted monomer, oligomers, and phosphate salts. The unreacted aniline concentration in the dialysis solution was determined by measuring the absorbance at 251 nm ($\epsilon = 151$)[31] in 1.0 M HCl. On the basis of the concentration of unreacted aniline, the percentage yield of PANI was calculated to be over 90%.

Each of the SPS/PANI samples used for the conductivity measurements were synthesized similarly except that a 3:1 ratio of aniline to SPS (24 mM aniline, 8 mM SPS) was used. To control the ratio of PANI to SPS in the complex, the amount of H_2O_2 added in the solutions varied from 6 mM to 20 mM. After the reaction, each sample was dialyzed against pH 4.3 deionized water overnight. By measuring the unreacted monomer in the dialysis solution, the molar ratio of produced PANI to SPS was calculated.

Precipitated PANI/SPS complex was prepared by polymerizing a 30 mL solution, which contained an excess of aniline monomer (6.0 mM SPS and 24.0 mM aniline). H_2O_2 was slowly added until dark green precipitates formed from the solution. The precipitate was then collected with a Buchner funnel, washed thoroughly with distilled water to remove any residual enzyme, phosphate salts, and unreacted monomer, and then vacuum-dried for 24 h for further characterization studies.

PANI/SPS Complex Characterization. The UV−vis spectra were recorded on a Perkin-Elmer Lambda-9 UV/vis/near-infrared spectrophotometer. FTIR measurements were carried out on a Perkin-Elmer 1760X FTIR spectrometer. For comparison, FTIR spectra were measured from both cast films of the PANI/SPS solution on AgCl crystals and from precipitated PANI/SPS using KBr pellets. The electrochemical characterization of the PANI/SPS was carried out on an EG&G potentiostat/galvanostat model 263. Cyclic voltammograms were recorded by using a three-electrode cell with a Pt wire as a counter electrode, a Ag/AgCl electrode as the reference electrode, and a platinum foil (1×1 cm^2) with a cast film of the PANI/SPS complex as the working electrode. An electrochemically grown polyaniline film was also prepared according to the method of Wei et al.[9a] and used for comparison. All cyclic voltammograms were carried out at room temperature in a 1.0 M HCl electrolyte solution and scanned between −0.2 V and 1.2 V at 100 mV/min. The conductivity of the PANI/SPS complex was measured using the four-probe method[19b] with a Keithley 619 electrometer/multimeter. The samples were prepared by casting the PANI/SPS complex solution on a glass plate and drying first in air and then under dynamic vacuum at 60 °C for 1 day to remove any residual moisture. The thickness of each film was measured on a Dektak II. In some cases the PANI/SPS complex films were additionally doped by a 4-h exposure to HCl vapor.

Molecular weight distribution of PANI/SPS complex was measured using gel permeation chromatography (GPC) with a Waters LC module I (Milford, MA) with two linear ultrahydrogel columns connected in series. A UV detector set at 218 nm was used to detect the polymer. Before the measurement, LiBr was added to each sample to a concentration of 1%. The sample solutions were filtered through 0.2 μm Millipore filters, and 0.15 μL of solution was loaded into the column. Phosphate buffer, pH 7.0, 0.1 M, was used as eluent, and a flow rate of 0.6 mL/min was maintained in each measurement.

Results and Discussion

Role of Template. To determine the role of the SPS template during the enzymatic polymerization, a series of control experiments were investigated. The polymerization was carried out in an 85% dioxane/15% water mixture with no SPS, an aqueous pH 4.3 buffered solution with no SPS, and an aqueous pH 4.3 buffered solution with 1 mM SPS. The dioxane solution was chosen here since this is a commonly used solvent system for enzymatic polymerization to obtain higher molecular weight polymers.[24a,b] To each solution, aniline and HRP were added to the concentrations of 1 mM and 30 μg/mL, respectively, prior to initiation. The polymerizations were then initiated with the addition of H_2O_2, and the progress of the reactions was monitored spectroscopically. In the case of the two solutions which did not contain SPS an immediate purple-colored solution was formed, whereas the solution which contained SPS immediately became a dark green color. As the reactions continued, the aqueous solutions without SPS became darker and eventually a brown precipitate was formed. The SPS solution, however, continued to become darker green with no observed precipitation.

The absorption spectra of the three solutions prior to precipitation were measured and are given in Figure 1. The solutions which contained no SPS showed an absorption band at approximately 460 nm, indicating the presence of multiple branched structures in the polymer.[25a] In contrast, the polyaniline formed in the presence of SPS exhibits a significantly different absorption spectrum. In this case, three absorption bands are observed which are consistent with the emeraldine salt form of PANI.[32] One is due to a $\pi-\pi^*$ transition of the benzenoid ring at 325 nm, and two absorption peaks at 414 and 843 nm are due to polaron band transitions.[32] These peaks indicate that a conducting form of the PANI, which is spectroscopically similar to that presently obtained through either chemical or electrochemical methods, may now be synthesized enzymati-

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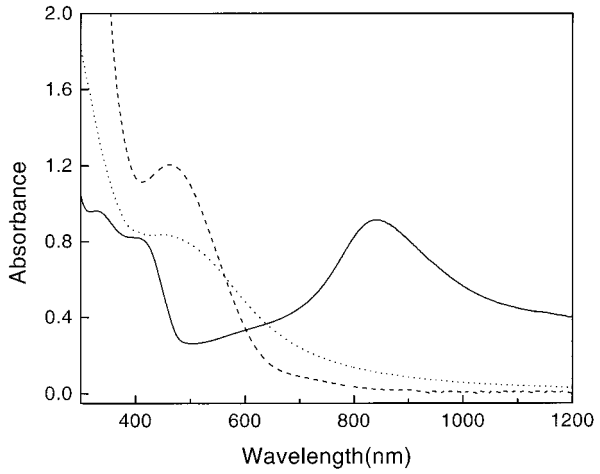

Figure 1. UV−vis spectra of the polymer obtained by the polymerization of 1 mM aniline in (···) phosphate buffer, (- - -)mixture of 85% dioxane and 15% buffer and (−)1 mM SPS buffer solution at pH 4.3.

cally. These results also demonstrate that the role of the template is critical to this process. The SPS in this case promotes a less parasitic and more para-directed polymerization, provides the necessary counterions for doping, and maintains the water solubility of the polyaniline.

A number of control experiments were also carried out to confirm that enzymatic catalysis is responsible for the polymerization. Here only hydrogen peroxide, that is, no enzyme, was added to the monomer solution, and it was found that no polymerization of aniline occured. Also, to rule out catalysis by Fe^{3+} from denatured HRP, $FeCl_3$ was used as the catalyst. It was found that under the same conditions, the observed percent conversions were insignificant in comparison to what is observed with the enzyme. These control experiments are strong evidence that the polymerization of aniline is due to HRP catalysis.

Effect of pH. The pH at which the enzymatic polymerization is carried out is very important in determining what type of polyaniline is ultimately formed (electroactive or insulating). The absorption spectra of PANI enzymatically synthesized with SPS at pHs ranging from 4.0 to 8.0 are given in Figure 2. At low pH (<5.50), the polymer shows strong absorption bands at 800−1060 nm and 410−420 nm which are again due to polaron transitions.[32] The intensity of the polaron bands at 800−1060 nm decreases with increasing pH and disappears when the pH of the reactant solution is greater than 6.0. At pH 5.5, a new peak emerges at 440 nm, which is again assigned to the formation of branched polymer.[25a] A bipolaron transition absorption band is also observed at approximately 737 nm at pHs 4.5−6.5 which is believed to be due to the presence of a fully oxidized PANI intermediate.[33,10b]

These results show that the enzymatic template polymerization of aniline is strongly pH dependent. A lower pH (4.0−4.5) is required to produce the conducting polyaniline, whereas a pH of 6.0 or higher results in a more branched, insulating form of polyaniline. This behavior may be explained by the aniline molecules being bound to the polyelectrolyte primarily through electrostatic attractive forces (although other short-range forces also contribute) which are both dynamic and pH dependent. In this local environment, the monomers remain mobile enough to interact with any enzyme, from the bulk solution, that comes in close enough proximity to the complex and be converted to free radicals for subsequent polymerization. The pH of the solution is critical in controlling the alignment

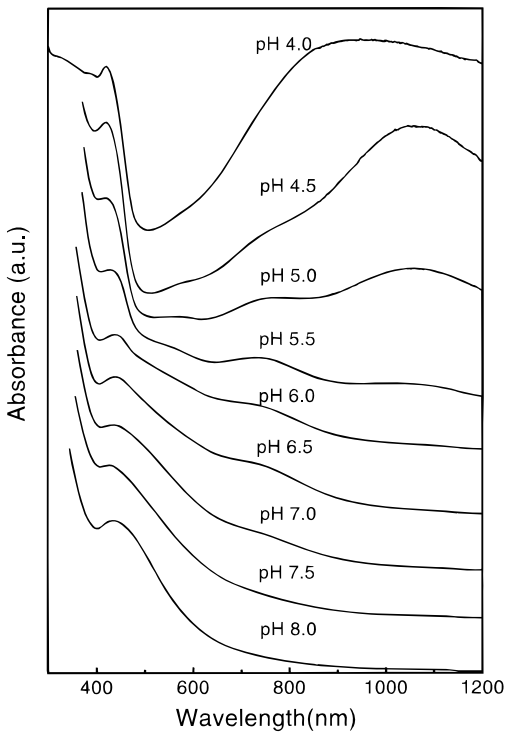

Figure 2. UV−vis spectra of the complex obtained by polymerization of a 1 mM aniline and 1 mM SPS system with pH ranging from pH 4.0−8.0.

of the aniline molecules in this molecular environment. At pH 4.0 most of the aniline monomer is positively charged (pK_a of 4.6) and the SPS is negatively charged (pK_a of 0.7). This difference in charge seems to promote a preferential alignment and salt formation of the monomer with the SPS, which results in the electrically conducting form of polyaniline. When the pH is raised above 4.65, this interaction is weakened due to the loss of positively charged aniline and a decrease in the proton concentration near the SPS molecules which is unfavorable to doping of the formed polymer. Even at a pH 4.5, a weak absorption peak is observed at 570 nm, which is due to the exciton transition of a quinoid ring in the undoped form of PANI.[32] It is also possible that as the pH is increased, the monomer alignment with the SPS is less than optimal for the head-to-tail coupling. Since HRP polymerization is known to be both ortho- and para-directed, the ortho coupling may become more dominate under these conditions and result in a more highly branched, insulating form of polyaniline as is typically observed with enzymatic polymerization of aniline. NMR studies are currently underway to establish the detailed mechanism of this polymerization.

This necessity for a "local" environment is further supported by preliminary studies designed to look at the effect of length or size of the template or matrix for the reaction. In these studies, polymerization was carried out using SPS of both 70 000 and 1 000 000 molecular weight. Comparison of the reactions using either molecular weight SPS however showed no observable difference. This suggests that both of these polymers are of sufficient size to provide the necessary local environment for electrostatic charging and alignment of the monomers. However, when these reactions are carried out with small molecules such as sodium benzenesulfonic acid (SBS), it is found that the conducting polyaniline is not formed at any concentration. These results show that the requisite "local" environment is provided by macromolecules such as SPS, but not by small, nonaggregating molecules such as SBS. Therefore, it seems that there is

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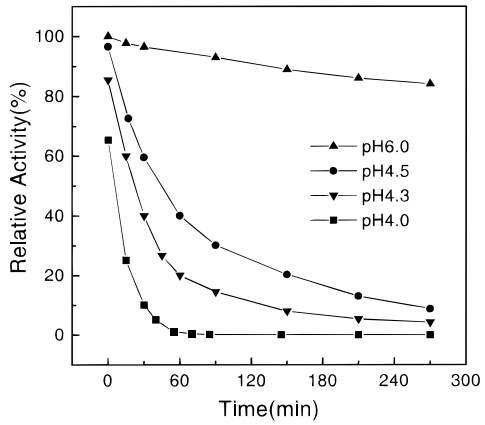

Figure 3. Time course of inactivation of HRP in aqueous buffer (▲) pH 6.0 (no sps), and with SPS (●) pH 4.5, (▼) pH 4.3, (■) pH 4.0. The initial activity of HRP in pH 6.0 phosphate buffer is regarded as 100% in the experiment.

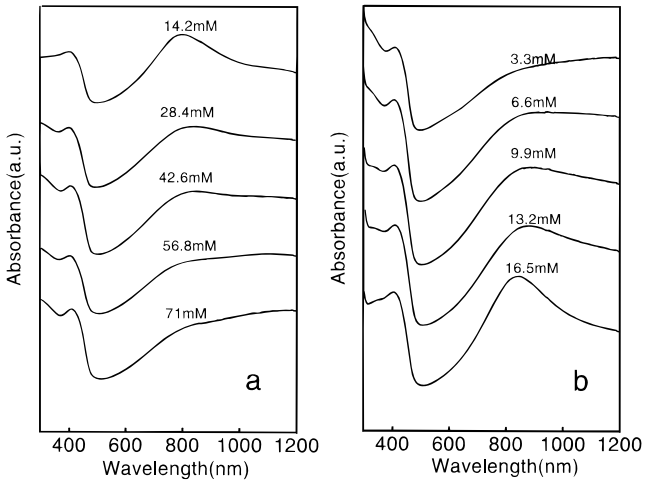

Figure 4. Effect of SPS and aniline concentration on the polymerization. UV−vis spectra of PANI synthesized in (a) varied concentration of aniline in pH 4.3, 30 mM SPS solution and (b) varied concentration of SPS in pH 4.3, 13 mM aniline solution.

a critical, limiting template molecular weight or size at which the electrically active form of polyaniline may be obtained using this approach. This limiting matrix size and the specific mechanisms of these reactions, however, are not clearly established and are currently under investigation.

The activity of the enzyme, HRP, is also pH dependent. The optimal pH for the catalytic activity of HRP is about pH 6.0. This activity decreases as the pH is lowered. Figure 3 shows a dependence of the activity of HRP, at room temperature, in 6 mM SPS solutions with the pH ranging from 4.0 to 4.5. Maximum reactivity at pH 6.0 was also measured for comparison. As shown, HRP maintains roughly 80% of its activity after 4.5 h in pH 6.0 phosphate buffer. However, as the pH is lowered, the activity of HRP quickly drops. For example at pH 4.0, only 20% of the original activity remains after 20 min, dropping to near zero activity at longer times. The enzyme activity significantly improves as the pH of the solution is increased. At a pH of 4.3 the enzyme activity is sufficient to provide both adequate activity of the enzyme and electrostatic interaction to form the emeraldine salt of polyaniline.

Effect of Aniline and SPS Concentration. The concentration and ratio of aniline and SPS in the solution also affects the type of polymer formed in the reaction. Figure 4a shows the absorption spectra of PANI/SPS complex synthesized with 30 mM SPS and various aniline concentrations. It is observed that, as the concentration of aniline increases, the polaron band at about 800 nm becomes broader and shifts to longer wavelengths, well into the infrared region. Since the absorption of the polaron band is strongly dependent on the molecular weight and protonation level of the PANI,[33] this indicates a difference in molecular weight of the polymer with concentration of aniline. It is believed that an increase in aniline concentration leads to more monomer aligning along the SPS template, which in turn is favorable to longer chain growth of the PANI. The effect of SPS concentration with 13 mM aniline was also studied, and the results are shown in Figure 4b. In contrast with the above results, as the concentration of SPS was increased, the polaron band absorption between 800 and 1200 nm becomes sharper with a distinct peak at 850 nm. In this case the increase of SPS molecules in the solution resulted in a dilution of aniline monomer on each SPS molecule. As a result, shorter PANI chains are formed. Thus, these data suggest that a higher molar ratio of aniline to SPS is favorable to longer chain growth and that shorter chain segments will form when the molar ratio of aniline to SPS is lower than that of 1:1.

The solubility of the PANI/SPS complex is very dependent on the composition of PANI and SPS in the solution. Since the solubility of the complex is due to the anionic charges on the SPS template, it is essential that enough of these charges remain to keep the complex in solution. Therefore, it was expected that if a sufficient number of charged sites on the SPS were neutralized by the PANI, precipitation of the complex would occur. This phenomenon of precipitation or "salting out" was observed when the ratio of aniline to SPS was brought up to 4:1. It was interesting to note that precipitation occurred at a specific point during the polymerization, whereby "snow-like" dark green precipitates formed, leaving behind a completely colorless supernatant. If more H_2O_2 was added after precipitation, the supernatant turned purple and in time precipitated, indicating that no SPS template was left for the aniline to template to. Since the PANI emeraldine salt is known to contain roughly 50% cationic charges along the backbone, it is possible that two PANI chains may be intertwined with a single SPS chain. This type of complex conformation has been previously shown for the chemical template polymerization of aniline.[34] Elemental analysis on the collected precipitate supports this type of complexation since the molar ratio of N/S was found to be approximately 2.3. Furthermore, as shown in Figure 5, the amount of H_2O_2 needed to form the PANI/SPS precipitate linearly increases with SPS concentration, suggesting a constant composition of PANI and SPS in the complex. Unlike the powder obtained by the evaporation of the complex solution, which can be easily redissolved in aqueous buffer, the precipitates formed during the reaction cannot be redissolved in aqueous solution, even in extreme low or high pH. This again supports the idea that neutralization of the SPS by a high content of PANI has occurred and recharging of the complex is not possible. These results also demonstrate true complexation in that the PANI/SPS behaves as one system rather than two separate species.

Characterization

GPC. The gel permeation chromatographs (GPC) of the complex solution were studied at different stages of the polymerization process. To eliminate the aggregation of mol-

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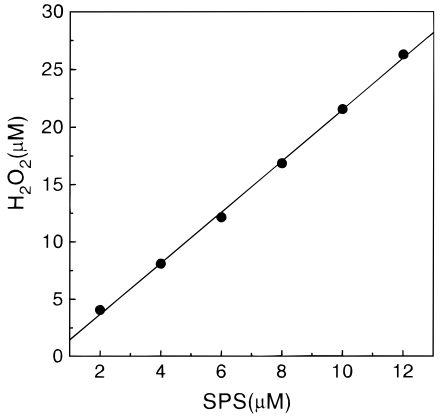

Figure 5. Linear relationship between the SPS and H_2O_2 needed to form the complex precipitate. The molar ratio of aniline to SPS in each polymerization reaction is 4:1.

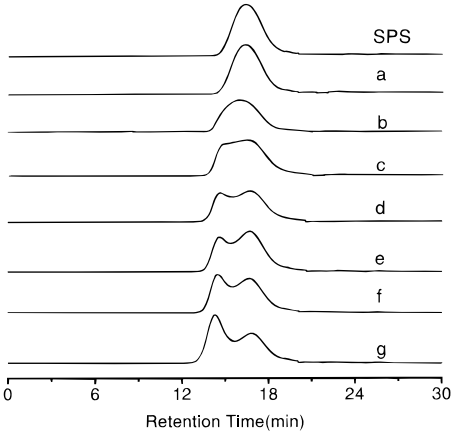

Figure 6. Gel permeation chromatographs of water-soluble PANI/SPS complexes which were obtained at different stages of the polymerization: (a) 20, (b) 40, (c) 60, (d) 80, (e) 100, (f)120, (g)140 min.

ecules, 1%(W/V) LiBr was added to each sample before the measurements. The results are shown in Figure 6. Given the complex nature of the PANI/SPS system, it is not possible to determine the molecular weight of the PANI alone, but trends in the chromatographs may be used to project complex formation and extent of polymerization. It is important to note that only one peak emerges as the reaction progresses and that this peak, which has a shorter retention time than SPS, shifts to shorter retention times. This is evidence that a complex is formed and that higher molecular weight species are formed with further polymerization. A number of authors have previously reported that the GPC curve of PANI base in NMP (*N*-methyl-2-pyrrolidone) exhibits a bimodal distribution with a major peak at low molecular weight and a minor peak at very high molecular weight.[35] In this case, in the initial stage of the reaction, no typical bimodal distribution is observed in the elution pattern for the PANI/SPS complex. The observed peak, with a retention time at 16.3 min is mainly due to SPS. As the reaction continues, a new peak at about 14.6 min emerges as a shoulder of the main peak. However, this two-peak pattern is quite different from that reported previously for pure PANI

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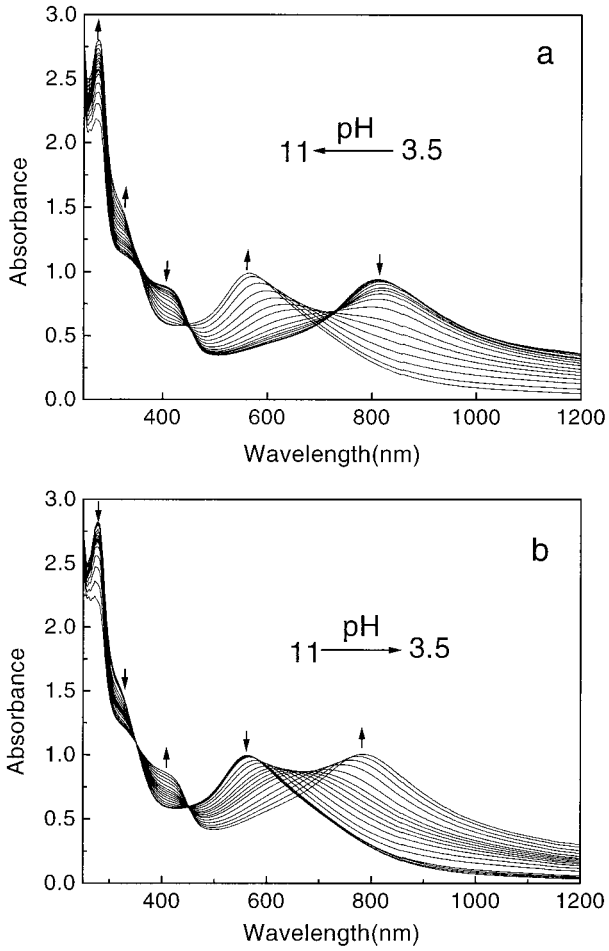

Figure 7. UV−vis spectra change of PANI/SPS complex during titration by 1 N NaOH and 1 N HCl. The pH ranged from (a) 3.5 to 11 and (b) 11 to 3.5. The pH was monitored by a pH meter during the titration.

which has been attributed to aggregation.[35] The peaks at the retention time of 14.6 min become larger and continue to shift to shorter retention times while the peak at 16.3 min decreases. It is believed that these observed changes are due to chain growth of polyaniline during the reaction, which results in the conversion of some lower molecular weight complexes to ones of higher molecular weight. Moreover, the chain growth of the PANI is not homogeneous on each SPS molecule. PANI with high molecular weight is initially formed as reflected by the peak at about 14.6 min. The fact that there is little deviation from the high molecular weight species indicates that the molecular weight of the complex is template dependent as proposed by Yang et al.[34]

Redox Reversibility. To determine the reversible redox behavior of the PANI/SPS complex, the absorption spectra of a complex prepared at pH 4.3 was studied with varying pH. Figure 7a gives the shift in absorption spectra of the complex with increasing pH from 3.5 to 11 by titrating with 1 N NaOH. At pH 3.5, the PANI in the complex is in the doped state as reflected by the presence of the polaron band transition at about 420 and 823 nm, as well as the $\pi-\pi^*$ transition of the benzenoid rings at 310−320 nm. As the pH of the complex is increased, the polaron bands at 420 and 823 nm gradually disappear, and a strong absorption due to exciton transition of the quinoid rings at 560−600 nm begins to emerge. At the same time bands at 257 and 320 nm, which are due to $\pi-\pi^*$ transitions of the benzenoid rings in the SPS and PANI molecules,[31] respectively, increase with a pH increase. At a pH

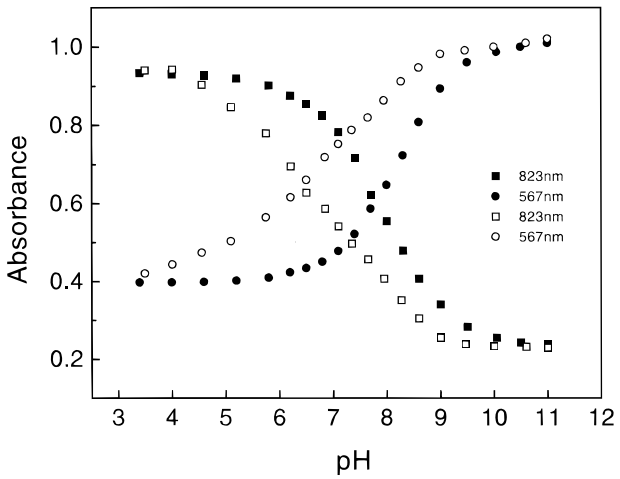

Figure 8. Variation of absorbances at 823 and 567 nm with the change of pH values. Curves with solid symbols (●) and (■) were for forward titration from pH 3.5 to 11, and curves with hollow symbols (○) and (□) were for backward titration from pH 11 to 3.5.

of 11, a blue solution of PANI/SPS complex is formed, indicating that the PANI has been fully dedoped to the emeraldine base form. The dedoped PANI can be redoped by titrating with 1 N HCl. A reversible color change is observed, and the spectra are given in Figure 7b. This pH induced redox reversibility confirms the presence of the electroactive form of polyaniline in the PANI/SPS complex. Furthermore, isobestic points at 353 and 457 nm can be observed clearly. However, the isobestic point at approximately 710 nm observed previously in a sulfonic acid ring-substituted PANI system,[19b,c] is not clearly seen in the present case.

The absorbances at 823 nm and at 567 nm for the above system are plotted against pH in Figure 8. In the case of titration with 1 N NaOH, the absorbance remains nearly constant from pH 3.5−6, indicating that the free proton in the solution is neutralized first. This is confirmed by the increase of the absorbance at 257 nm at initial titration which is due to the neutralization of the free proton in the vicinity of SO_3^{2-}. The oxidation of PANI in the complex starts at about pH 6.0, and most of the PANIs are still in their doped states even at pH 7.5. In contrast, the chemically synthesized PANI is usually dedoped at pH 4.[10b] This retention of the doped state at higher pH is due to the high concentration of protons in the vicinity of the PANI backbone provided by the SPS molecules.[18b] The decrease of the 823 nm band and the increase of the 567 nm band signify the transformation of the benzenoid into quinoid rings. At pH 9.5, PANI in the complex is fully dedoped, and the absorbance is constant with the continuous increase of pH. It is interesting to note that the absorbance at 824 and 567 nm present a hysteresis loop during the titration from pH 3.5−11 and back from pH 11−3.5. The origin of the hysteresis loop and the disappearance of the isobestic point at 717 nm is believed to be due to the strong interaction between the PANI and SPS molecules, which causes a pronounced delay in the redox process.[34]

FTIR. Figure 9 shows the FTIR spectra of a PANI/SPS complex solution and the precipitate in the region from 2000 to 400 cm^{-1}. It is clear that these spectra can be superimposed with the only difference being that the infrared spectra from a cast solution exhibits sharper peaks. The bands at 1584 and 1484 cm^{-1} are due to quinone and benzine ring deformation,[36] and the band at 1310 cm^{-1} is assigned to C−N stretching of a secondary aromatic amine.[37] The C−H out-of-plane bending located at 830 cm^{-1} in both spectra is due to a para-substitution

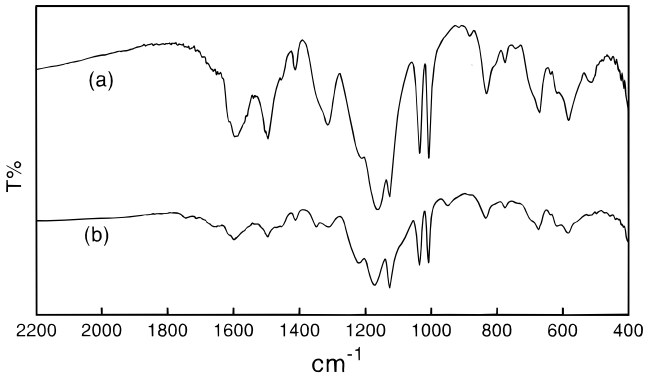

Figure 9. FTIR spectra of (a) solution and (b) precipitate of PANI/SPS complex.The solution was measured by casting a film on a AgCl crystal window. The precipitate spectrum was obtained using a KBr pellet.

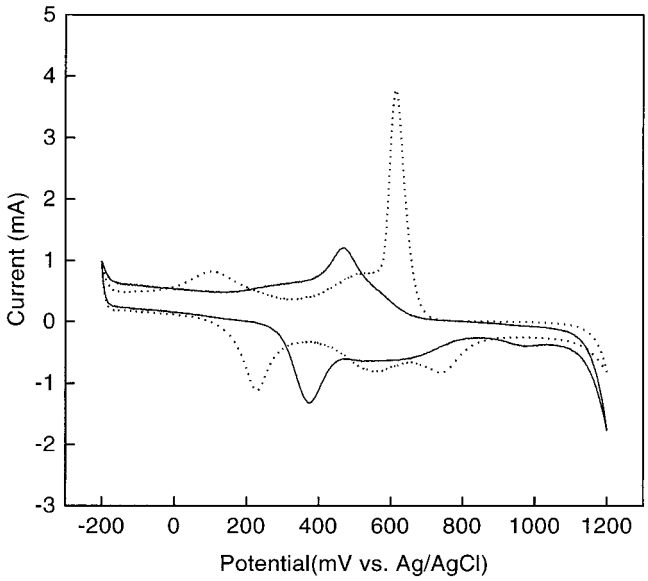

Figure 10. Cyclic voltammograms of (- - -) electrochemically deposited PANI film and (−) a solution cast film of PANI/SPS in 1 M HCl with a scan rate of 100 mV/s.

pattern, indicating that a head-to-tail coupling of aniline occurs during the polymerization.[37] No bands due to other substitution patterns (meta, ortho) are clearly observed. These FTIR spectra are in good agreement with spectra obtained from chemically synthesized PANI. A closer inspection of the relative intensities at 1584 and 1484 cm^{-1} shows that much of the PANI is in the doped state for both the solution cast film and the precipitate. In addition, the presence of asymmetric and symmetric S═O stretching bands at 1034 and 1008 cm^{-1} for both samples confirms the presence of SPS in the complex.[19c,38]

Cyclic Voltammetry. The electrochemical nature of the PANI in the PANI/SPS complex was determined by using cyclic voltammetry. Figure 10 shows the cyclic voltammograms (CV) of a cast film of the complex compared to an electrochemically grown PANI. The electrochemically grown PANI film was deposited by cycling the potential between −0.2−1.2 V vs Ag/AgCl. Three sets of redox peaks are observed with the $E_{1/2}$ at 0.17, 0.51, and 0.67 V, which are similar to previous reports.[9a,39]

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(37) Tang, J. S.; Jing, X. B.; Wang, B. C.; Wang, F. S. *Synth. Met.* **1988**, *24*, 231.

(38) Chen, S.-A.; Hwang, G.-W. *Polymer* **1997**, *38*, 333.

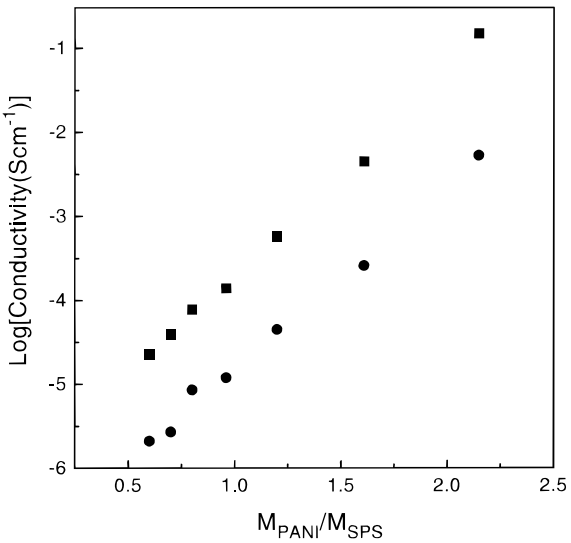

Figure 11. Plot of log(conductivity) as a function of the molar ratio of PANI to SPS in the complex (●) before and (■) after additional doping with HCl vapor.

The peak at 0.51 V disappears when cycling the potential between −0.2−0.8 V during the preparation. Typically, two sets of redox peaks are observed with electrochemically grown and chemically prepared PANI.[39] The PANI/SPS complex, however, displays only one set of redox peaks at $E_{1/2} = 0.43$ V over the full potential window from −0.2 to 1.2 V. Similar results were observed by Chan and co-workers for poly(*o*-aminobenzylphosphonic acid) which showed only one redox peak at $E_{1/2} = 0.39$ V.[40] This peak was assigned as the first redox wave in the parent PANI. The absence of the second redox process, as in our case, is believed to be due to the exceptional resistance of the PANI to oxidation to the pernigraniline state.

Conductivity. To determine the effect of SPS on the conductivity of the complex, a series of samples with varying molar ratios of PANI/SPS were synthesized and cast as bulk films for conductivity measurements. In each case, the conductivity of the pure complex was measured, and then the same film was exposed to HCl vapor for additional doping. A plot of conductivity versus molar ratio of PANI/SPS for each sample before and after exposure to HCl is given in Figure 11. As shown and as expected, the conductivity increases with the concentration of PANI in the complex. As the molar ratio of PANI/SPS increases from 0.6 to 2.2, the conductivity increases almost 4 orders of magnitude and reaches a maximum conductivity of 5.3×10^{-3} S/cm. After exposure to HCl vapor, the conductivity of each of the samples increases another 1−2 orders of magnitude and reaches a maximum conductivity of 0.15 S/cm for the highest PANI containing complex. The observed conductivity of PANI/SPS complex is somewhat lower than that obtained with pure chemically synthesized PANI (1−10 S/cm)[32a] but higher than that of polymer formed from some *N*-substituted anilines (10^{-3}−10^{-7} S/cm),[17] and is comparable to sulfonated PANI (0.1 S/cm).[18b] This lower conductivity may be attributed to the presence of the insulating SPS component.

The observed increase in conductivity upon exposure to HCl vapor indicates that the PANI in the complex is not in the completely doped state. The sulfonic counterion groups on the SPS have an effective diameter of approximately 11 Å.[18b] In comparison with a sulfonated PANI in which the SO_3^{2-} groups are covalently bonded to the aromatic rings,[18b] the present case has counterions that form an intermolecular electrostatic complex. This complex may not provide for optimal complexation of the counterions because of steric restrictions. The undoped percentage of PANI in this case is believed to be very low since relatively high conductivities were observed in the film even before additional doping.

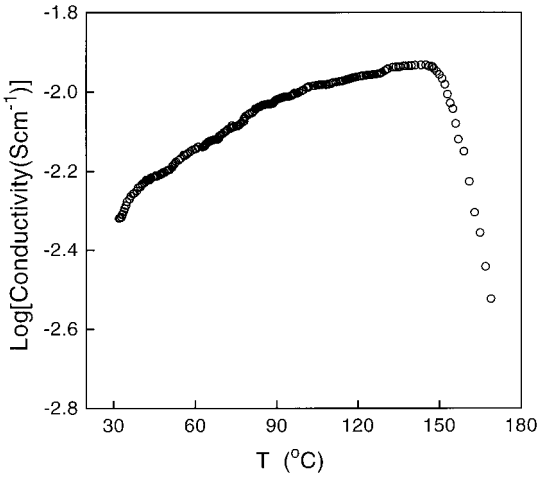

Figure 12. Plot of log(conductivity) as a function of temperature from 20 to 170 °C.

The temperature dependence of the conductivity for the complex is shown in Figure 12. The conductivity increases with temperature from 20 to 145 °C and then decreases from 145 to 170 °C. The conductivity drop above 145 °C is attributed to thermal dedoping. The temperature of thermal dedoping of the complex is lower than that observed for sulfonated PANIs which occurs at 190 °C [19c] and is 20 °C higher than that reported for a blend of sulfonated PANI with poly (vinyl alcohol) (occurred at 110 °C).[38]

Conclusion

A unique, biological route for the synthesis of water soluble, conducting polyaniline is presented. This approach is particularly attractive in that it is simple (one step), uses very mild conditions (pH 4.3), and requires minimal separation and purification. This approach is also significant in that it demonstrates a new way to optimize enzymatic polymerizations. By controlling the electrostatic charges of the monomer and a suitable template, problematic parasitic branching of the polymer is obviated and a head-to-tail coupling of the aniline prevails. Variation of the concentration ratio of the aniline and template also allows for control over the resultant conductivity of the complex. These results suggest new possibilities in the manipulation of biological materials as potential matrixes, which may lead to the development of novel biological sensors, biomimics, and possibly new ways to probe complex biological templates. Last, this approach is general in that various comonomers and templates may be interchanged to produce important electroactive polymers.

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