An Enzymatically Synthesized Conducting Molecular Complex of Polyaniline and Poly(vinylphosphonic acid)

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ABSTRACT: Enzymatic synthesis of a conducting complex of polyaniline (PANI)−poly(vinylphosphonic acid) (PVP) is presented. The polymerization of aniline was carried out in an aqueous buffer at pH 4.0 using the enzyme horseradish peroxidase (HRP) as the biocatalyst in the presence of a PVP polyanion template. The formation of the conducting and electroactive form of the PVP−PANI complex was confirmed through UV−vis and FTIR spectroscopy, elemental analysis, four-point probe conductivity measurements, and thermogravimetric analysis. Appropriate control of polymerization could be used to tune the water solubility and conductivity of the final PVP−PANI macromolecular complex. This template-guided enzymatic reaction is a unique approach for the controllable polymerization of aniline to the electroactive form under milder and environmentally compatible conditions. In this work, PVP was chosen as the polyelectrolyte to demonstrate both versatility with other templates and as a proof-of-concept for extension of this approach to other more delicate phosphate/phosphonic acid containing biological polyelectrolytes such as DNA.

Introduction

The field of inherently conducting polymers has attracted considerable attention due to their interesting electrical and optical properties for many technological applications. Polyaniline (PANI) has been one of the most extensively investigated conducting polymers because of its excellent stability and promising electronic properties. The potential for the use of polyaniline in a wide range of applications including electrochromic devices,[1] light-emitting diodes,[2] electrostatic discharge protection,[3] lightweight batteries,[4] and corrosion protection, among others, has already been demonstrated. However, commercial application of PANI has been limited due to the severe chemical conditions involved in the synthesis and the tedious purification and separation procedure(s), which often lead to an intractable polymer.

Numerous approaches have been investigated to address these limitations including the exposure of PANI to protic acids in aqueous solution,[5−7] the use of phosphoric acid esters for the protonation of polyaniline,[8] and the synthesis of highly sulfonated forms of polyaniline such as leucoemeraldine base-sulfonated polyaniline (LEB−SPAN).[9] Other approaches have involved the use of substituted aniline monomers, which can be polymerized either chemically,[10,11] electrochemically,[12] or biochemically[13] to give self-doped PANI, including alkyl[14] and alkoxy[15] ring substituted polyanilines. In general, however, the molecular weight of these polymers is quite low, and the electronic properties are poor. Polymeric protonating agents have also been used as polydopants,[16] for the synthesis of solution processable conducting PANI. These methods of synthesis however usually involve laborious preparation and harsh synthetic conditions including a low-pH environment, and the resulting polymer/polymer composites lose electroactivity on prolonged exposure to neutral-pH conditions.

Other studies have involved the use of a polyelectrolyte template to align the monomer molecules, which could be subsequently chemically or electrochemically polymerized.[17−19] Here the anionic polyelectrolyte template provides charge compensation to the protonated PANI and imparts water solubility to the final molecular PANI−polyelectrolyte complex. These approaches have significantly improved the solubility and processability of PANI and PANI complexes; however, the harsh reaction conditions remain. Enzymatic reactions have therefore been investigated as an alternatively mild and environmentally compatible approach to the synthesis of conducting polyaniline. Horseradish peroxidase (HRP) has been used as a catalyst for the synthesis of polyphenols and polyanilines.[20,21] The reaction involves an initial two-electron oxidation of the native ferric enzyme to an oxidized intermediate (HRP-I) by hydrogen peroxide. The aniline monomer is oxidized by the HRP-I to produce monomeric radical species, which then undergo coupling to form dimer. Successive oxidation and coupling reactions eventually result in the formation of polymer. The regeneration of the native peroxidase is accomplished by two sequential one-electron reductions through a partially oxidized intermediate (HRP-II). The periodic cycle results in the oxidation of a variety of electron donors such as phenols and aromatic amines. This enzymatic synthesis however is limited in that only low molecular weight oligomers that have very poor electrical properties may be formed under aqueous conditions.[22]

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Recently, we have reported on a unique enzymatic technique that resolves the limitations of both chemical and enzymatic polymerization of aniline.[23] In this approach, aniline monomers are preferentially dispersed in a sulfonated polystyrene (SPS) template under aqueous conditions. This template provides a type of nanoreactor that serves to both emulsify the aniline and provide a localized lower pH environment that promotes the para-directed coupling of the aniline monomers.[24] The final product is a water-soluble, conducting molecular complex of PANI/SPS. The versatility of this biochemical approach to a range of other interesting polyelectrolytes suggests exciting opportunities in the synthesis of new polyanilines. In particular, the extreme mildness of this enzymatic approach is expected to allow for the use of more delicate phosphate-based biological materials as templates.

Organic phosphates/phosphonic acids are present in numerous biologically derived polyelectrolytes. Phospholipids and sterols make up approximately half the mass of biological membranes. Previous work toward the complexation of phosphate-based materials with PANI has included poly(alkylene phosphates) as dopants mixed with PANI in *N*-methylpyrrolidone solution.[25] The PANI however used in these cases has been chemically polymerized before the introduction of the dopant. These systems are not water based and are also prone to spontaneous deprotonation/undoping. Polyaniline has also been synthesized chemically under low-pH conditions, in the presence of poly(vinylphosphonic acid) (PVP).[26] Although these approaches have been successful toward the polymerization of phosphate-based PANI complexes, the harsh chemical conditions preclude the use of more delicate biological-based phosphate materials as templates. The enzymatic approach however offers much more biocompatible synthetic conditions. The purpose of this study therefore is to investigate the synthesis of a molecular complex of polyaniline and organic phosphates/phosphonic acids in aqueous solvents but under the much milder, near neutral-pH conditions used with the enzymatic approach. This selection of PVP as the polyelectrolyte for the polymerization of aniline is an important preliminary step toward extending this approach to other biologically derived polyelectrolytes such as DNA.

Experimental Section

Materials. Horseradish peroxidase (HRP, EC 1.11.1.7) type II, 150−200 units/mg solid, was purchased from Sigma Chemical Co. (St. Louis, MO). The concentration of HRP stock solution in most cases was 5 mg/mL. Poly(vinylphosphonic acid) was obtained from PolySciences Inc. and used as received. The number-average molecular weight, M_n, and the weight-average molecular weight, M_w, as provided by PolySciences Inc. were 19 500 and 24 100 Da, respectively. Aniline monomer (purity 99.5%) and hydrogen peroxide (30 wt %) were purchased from Aldrich Chemicals Inc., Milwaukee, WI, and were used as received. The hydrogen peroxide was diluted to 0.3% (in deionized water), and this solution was used for polymerization. Spectra-pore dialysis membrane was purchased from Fisher Scientific, Springfield, NJ. All other chemicals were of reagent grade or better.

Polymerization. All polymerization reactions were carried out enzymatically at room temperature, in 10 mM sodium phosphate buffer at pH 4.0. The calculations on molar ratios were based on the molecular mass of the repeat unit in the case of PVP.

Water-Insoluble Complex (PVP−PANI-I). A 100 mg sample of PVP was dissolved in 9.3 mL of sodium phosphate buffer to give a 100 mM PVP solution. To this solution was added 84.3 μL of aniline with constant stirring. The pH of the solution was monitored and adjusted to 4.0. To this solution was added 10 mg (200 units/mg) of HRP. The polymerization was initiated by the addition of 0.3% hydrogen peroxide. It was observed that the polymerization depends on both the amount and the rate of addition of hydrogen peroxide. Further, it has also been reported earlier that addition of excess H_2O_2 will cause inhibition of the enzyme.[27] Hence, H_2O_2 was added in small amounts (10 aliquots of 100 μL each) with a time interval of 2 min between each addition. The reaction mixture was stirred for 4 h to ensure completion of the polymerization process. The mixture containing the dark green PVP−PANI precipitate was filtered through a 1 μm nuclepore track-etch membrane and washed repeatedly with 1:1 acetone/deionized water solution for the removal of unreacted aniline monomer and enzyme. The precipitate was then dried in a vacuum oven at 60 °C for 48 h and used for further characterization. The gravimetric yield was approximately 78%.

Water-Soluble Complex (PVP−PANI-S). The method adopted for the synthesis of PVP−PANI-S was similar to the synthesis of PVP−PANI-I, except the total amount of hydrogen peroxide added was limited to 65 μL (10 aliquots of 6.5 μL each). The reaction mixture was left stirring for 4 h, and the PVP−PANI-S complex remained soluble. The final solutions were transferred to individual regenerated natural cellulose membrane bags (molecular weight cutoff 1000 Da) and were dialyzed against 5 L of acidified deionized water maintained at pH 4.0. Dialysis was carried out for 72 h with fresh acidified deionized water being added every 12 h to expedite the removal of oligomers and unreacted monomer. The PVP−PANI-S complex was precipitated by adding a large excess of acetone and then filtered through a 1 μm membrane filter. The precipitate was washed several times with pH 4.0 deionized water and dried in a vacuum oven at 60 °C for 48 h. PVP−PANI complexes were also synthesized in 10 mM citrate buffer for the purpose of elemental analysis in order to avoid the interference of phosphorus from the buffer solution.

Optimization of the Synthetic Conditions for the Water-Soluble PVP−PANI Complex. To follow the extent of polymerization and optimize the conditions, a series of 12 reactions were carried out in this study. All reaction systems contained 10 mL of 10 mM phosphate buffer, 13.7 μL (15 mM) of aniline, and 2.5 mg of HRP. The PVP concentration was varied between 0.6 and 375 mM. A 0.3% H_2O_2 solution was used in each case, and 25 μL of this solution was added at 90 s increments until precipitation was observed. All reaction mixtures were magnetically stirred for 1 day and then filtered through a 1 μm filter and washed several times with 1:1 acetone/water and dried at 60 °C in a vacuum oven for 24 h before being weighed.

Characterization of PVP−PANI Complexes. UV−vis−near-IR spectra of dilute solutions (0.3 mg/mL) of the PVP−PANI-S were obtained using a Perkin-Elmer Lambda 9 spectrophotometer. FT-IR measurements were carried out using a Perkin-Elmer 1720X series FT-IR spectrophotometer. Conductivity measurements were carried out on PVP−PANI pressed pellet samples using a Cascade Microtech four-point probe connected to a current source and electrometer. The conductivity values reported are the average of several readings at different regions and sides of the disk. The variation in the measurements made at various areas of the sample was within 10% of the mean reading. Thermogravimetric analysis (TGA) was performed using a TA Instrument, Hi-Res 2950 thermogravimetric analyzer. The TGA of all samples were carried out in a nitrogen atmosphere. The analysis of elemental carbon, hydrogen, nitrogen, and phosphorus in PVP−PANI and PVP was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Results and Discussion

PVP was found to be a suitable template in the enzymatic polymerization of aniline. Similar to the SPS template reported previously, the PVP template pro-

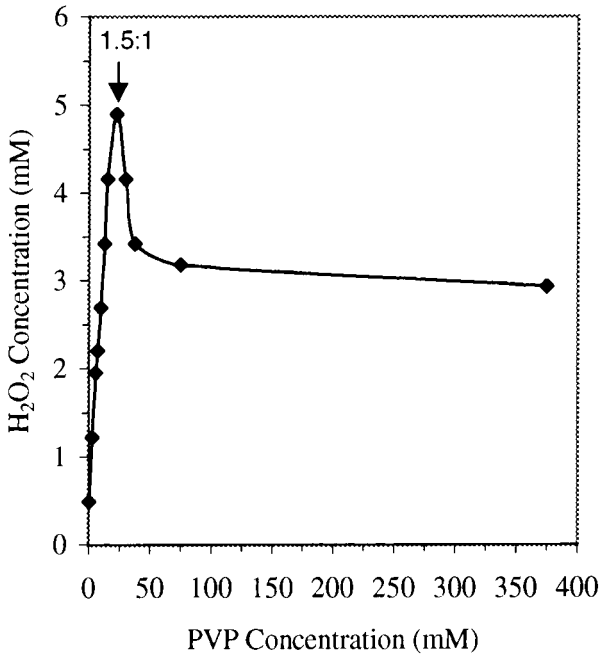

Figure 1. PVP concentration versus H_2O_2 concentration required for precipitation of the PVP−PANI complex.

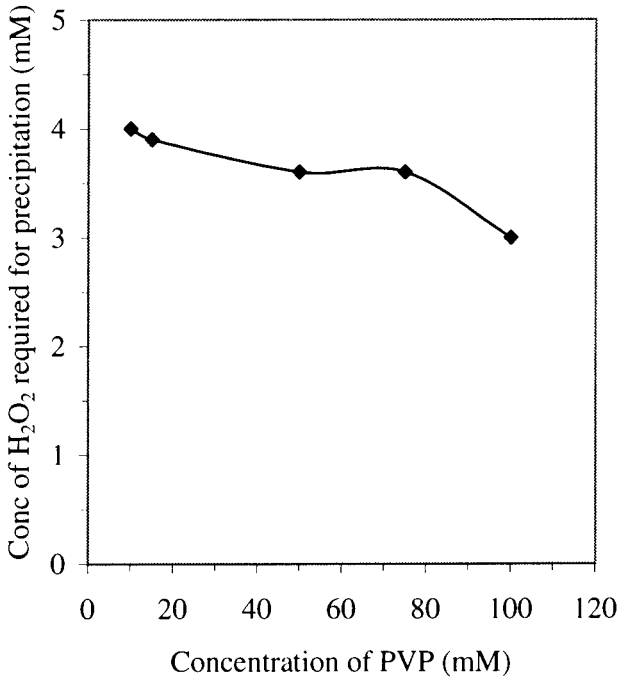

Figure 2. Concentration dependence of PVP−PANI precipitation.

motes the para-directed polymerization and provides the requisite counterions for doping to the emeraldine salt form of polyaniline.[23] However, unlike previous studies, it was found that the PANI−PVP complex precipitates or "salts out" of solution at specific stoichiometric ratios of PANI to PVP. Therefore, in an attempt to optimize the conditions required for maintaining the complex in a soluble form, as well as for determining the ratio of phosphonic acid repeat unit to aniline repeat unit in the complex just prior to precipitation, a matrix of reaction systems was set up. In these experiments, the molar ratio of phosphonic acid repeat unit:aniline in the reaction medium was varied from 0.04:1 to 25:1, while the amount of enzyme was kept constant in all cases. The reaction was controlled by incremental addition of H_2O_2 until the onset of precipitation. Figure 1 is a plot of the amount of H_2O_2 required to precipitate the PVP−PANI complex with 15 mM aniline in the reaction medium, while varying only the concentration of PVP. These results show that the amount of H_2O_2 required for precipitation increases linearly when the aniline concentration is lower than the PVP concentration, up to a maximum ratio of 1.5:1 (PVP:aniline). After this maximum ratio, however, the amount of H_2O_2 required for precipitation decreases and then eventually levels off as the PVP:aniline ratio continues to increase.

Considering the mechanism of HRP-catalyzed polymerization, it is reasonable to expect a linear relationship between the amount of H_2O_2 added and the amount of aniline radicals formed.[28] However, in this case, when the molar ratio of phosphonic acid repeat unit:aniline is increased beyond the 1.5:1 peak ratio, the excess PVP in the system is no longer able to contribute to the solubility of the complex. Assuming that the amount of H_2O_2 corresponds to the amount of polymer formed, the slope of this linear portion of the curve gives a molar ratio of approximately 5:1 for PVP to PANI. These results suggest that in the linear region of the curve the PVP−PANI precipitate has a constant composition of PVP and PANI.

Table 1. PVP

element	expt (%)	theor (%)	error (%)
carbon	22.52	22.24	1.26
hydrogen	4.68	4.68	0
phosphorus	24.50	28.67	−14.54
oxygen[a]	48.30	44.41	8.76

[a] By difference.

This concentration dependence of precipitation was also studied in the range of 10−100 mmol of PVP. A ratio of 1:1, PVP:aniline, was maintained in this study. The goal of this experiment was to determine whether the high PVP concentration regime (>50 mM) was contributing to the precipitation. The data presented in Figure 2 suggest that even at high PVP concentration, there is only a marginal change in the amount of H_2O_2 required to cause precipitation. This indicates that in the previous experiment (Figure 1), when the concentration of PVP was greater than 50 mM, the high concentration of PVP was not contributing to the precipitation of the complex.

Elemental Analysis. The results from estimation of elemental (percent) carbon, hydrogen, nitrogen, and phosphorus for PVP and the corresponding theoretical values are presented in Table 1. The error in the amount of elemental phosphorus may be explained by the presence of residual chlorides, used in the synthesis of PVP, which could result in the apparent decrease in the phosphorus content. Hence, these (experimental) values were used for the theoretical calculation of the percentage of elemental carbon, hydrogen, nitrogen, and phosphorus in the PANI−PVP-I and PANI−PVP-S to correct for this difference. Comparisons of the experimental results of the elemental analysis with theoretical values representing the possible ratios of phosphonic acid repeat unit to aniline repeat unit are presented in Tables 2 and 3.

In the case of PVP−PANI-I, the ratio of phosphonic acid repeat unit to aniline repeat unit is found to be nearly 1:1. If a stoichiometric ratio of 0.9:1 aniline:

Table 2. PVP−PANI-I

element	expt 1:1 (%)	theor 1:1 (%)	theor 0.9:1 (%)	error 1:1 (%)	error 0.9:1 (%)
carbon	49.45	48.29	49.79	2.39	−0.68
hydrogen	5.20	5.05	5.07	3.01	2.58
nitrogen	7.69	7.03	7.44	9.35	3.42
phosphorus	12.07	13.28	12.64	−9.14	−4.52
oxygen[a]	25.59	26.34	25.07	−2.85	2.09

[a] By difference.

Table 3. PVP−PANI-S

element	expt (%)	theor 1.50:1 (%)	theor 1.71:1 (%)	error 1.5:1 (%)	error 1.71:1 (%)
carbon	38.73	42.74	41.05	−9.38	−5.66
hydrogen	4.99	4.97	4.95	0.41	0.90
nitrogen	5.08	5.53	5.08	−8.18	0.05
phosphorus	16.14	15.68	16.40	2.96	−1.60
oxygen[a]	35.06	31.08	32.52	12.79	7.80

[a] By difference.

phosphonic acid repeat unit is assumed and the theoretical amounts of elemental carbon, hydrogen, nitrogen, and phosphorus are estimated, we find that these theoretical values are closer to the values determined by elemental analysis. This higher molar ratio of the aniline repeat unit to the phosphonic acid repeat unit supports the higher propensity of the complex to precipitate.

The results of the elemental analysis for PVP−PANI-S in Table 3 provide information on the ratio of the phosphonic acid repeat unit to the aniline repeat unit at the precipitation threshold (immediately prior to precipitation). It is evident from the data in Table 3 that the ratio of phosphonic acid repeat unit to aniline repeat is significantly higher than that for the PVP−PANI-I. This suggests that ratios as high as 1.7:1 (phosphonic acid to aniline) are necessary to maintain solubility in the complex. This result compares well with the data presented in Figure 1, where it was shown that a ratio of approximately 1.5:1 phosphonic acid repeat unit:aniline repeat unit could accommodate a maximum amount of PANI and yet remain soluble. This elemental analysis data obtained from the PVP−PANI-S complex further supports the existence of a constant ratio of PVP to PANI just prior to the complete neutralization (salting) of PVP by the PANI.

For the purpose of further characterization and analysis, a molar ratio of 1:1 PVP:aniline was used in the reaction medium, and the amount of H_2O_2 varied according to the procedure outlined earlier for the synthesis of PVP−PANI-I and PVP−PANI-S.

Doping−Dedoping Reversibility of PVP−PANI. PVP−PANI-S was used for studying the reversible redox behavior of the polyaniline in the complex, and the results are presented in Figures 3 and 4. The UV−vis−near-IR spectra of the PVP−PANI-S obtained at pH 4 shows some similarity to the spectra reported earlier for the SPS/PANI complex.[23] The polaron band at 420 nm as well as the $\pi-\pi^*$ transition of the benzenoid rings at 310 nm confirms the presence of PANI in the doped state. In the case of the PVP−PANI, another long wavelength polaron band appears at 1000 nm. This band was previously observed at a wavelength of 823 nm with the SPS−PANI complex. It is also interesting to note that this band is completely absent in the case of chemically synthesized PVP−PANI previously reported in the literature.[26] This shift of the polaron band to longer wavelengths has been reported earlier for

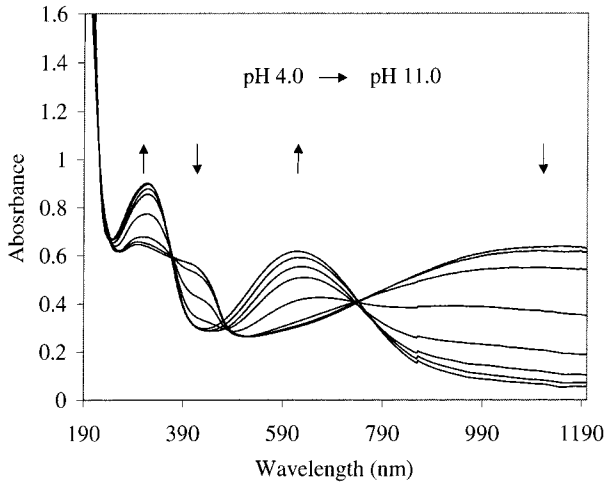

Figure 3. Dedoping of PVP−PANI-S (pH 4.0−pH 11.0).

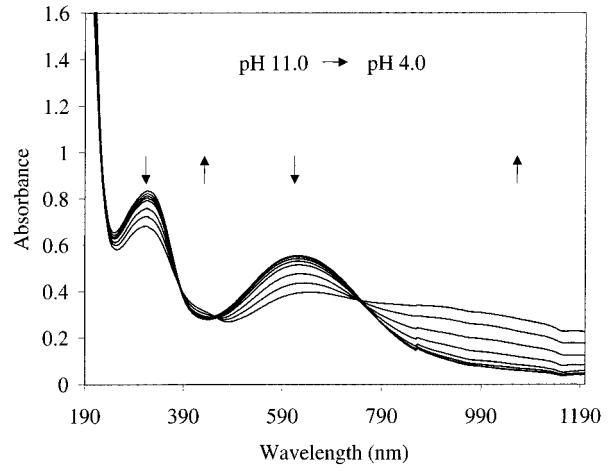

Figure 4. Redoping of PVP−PANI-S (pH 11.0−pH 4.0).

electrochemically polymerized PANI and is attributed to the differences in the oxidation states (polaron or bipolaron) of the polymer.[29]

When the pH of the solution is increased from 4 to 11 using NaOH solution, a decrease and subsequent disappearance of the polaron bands at 420 and 1000 nm is observed. Simultaneously, the emergence of absorption in the 600 nm region is observed and attributed to the exciton transition of the quinoid rings. The 260 and 320 nm bands assigned to the $\pi-\pi^*$ transition of the benzenoid rings in PANI also increases with the increase in pH. At pH 11, the PANI is completely dedoped to give PANI base, and the absorption spectrum is comparable to chemically synthesized PVP−PANI base reported earlier.[26] Two isosbestic points at 485 and 745 nm are also observed and found to be shifted to higher wavelengths as compared to previous reports of 457 and 710 nm for the SPS/PANI and sulfonic acid ring-substituted PANI system,[5] respectively. These doping/dedoping processes are fairly reversible as seen by partial restoration of the original doped PANI spectrum in Figure 4 and appear to be time dependent. Higher levels of restoration of the polaron bands are observed if the absorption spectra are recorded after several hours. In the case of the SPS−PANI complex it has been reported that complete restoration of the polaron bands occurs immediately.[23] This difference in behavior may be explained by the pK_a of the phosphonic acid repeat unit. The pK_a of the benzenesulfonic group in SPS is much lower than that of the phosphonic acid group in

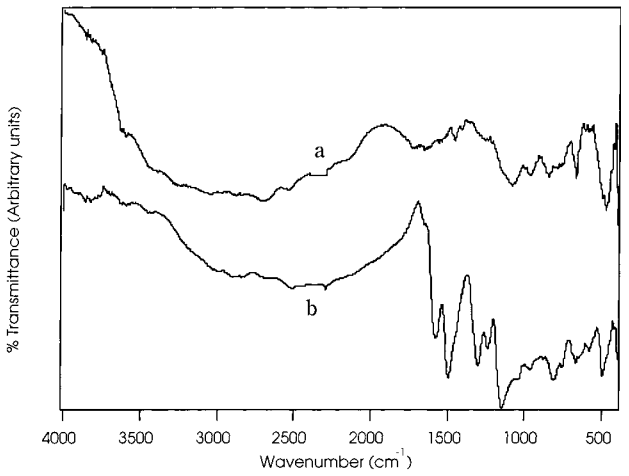

Figure 5. FTIR spectra of PVP (a) and PVP−PANI-I (b).

Table 4. Conductivity (S/cm)

conditions	PVP−PANI-I	PANI-A
after desiccation	5.5×10^{-2}	7.8×10^{-1}
after 1 h at 110 °C	4.3×10^{-2}	6.7×10^{-1}
after 4 h at 150 °C	2.3×10^{-2}	4.3×10^{-1}
after 15 h at 150 °C	1.2×10^{-2}	3.1×10^{-1}

PVP.[23,24] Therefore, at pH 4, the PVP is less dissociated when compared with the SPS. Hence, the extent of redoping could vary on the basis of the polyelectrolyte matrix. These results demonstrate the formation of a water-soluble, electroactive polyaniline using PVP as the template.

FTIR. The FTIR spectra of PVP and PVP−PANI-I are shown in Figure 5. The ring stretch of the polyaniline quinoid form is observed as a broad band at 1580 cm^{-1}, while the ring stretch of the benzenoid form appears as a significantly broad band centered around 1497 cm^{-1}. The in-plane bending vibration of the aromatic hydrogen at 1165 cm^{-1} combined with intense absorption of the phosphonate ion appears as a broad band centered around 1150 cm^{-1}. However, this band is clearly distinct and different from the one observed in the case of PVP. The presence of the P═O vibration band at 917−1040 cm^{-1} in both PVP and PVP−PANI-I spectra confirms the presence of the template in the complex. The presence of PVP in the complex is more clearly discernible in the enzymatically synthesized PVP−PANI.

Conductivity Measurements. The conductivity of both PVP−PANI-I and PVP−PANI-S was measured using a four-point probe. PVP−PANI complexes were dried in a vacuum oven at 60 °C for 48 h, desiccated, and then compacted into a pellet using a standard IR die in a hydraulic press. The hygroscopic nature of PVP necessitates drying in a desiccator for several weeks prior to carrying out the conductivity measurements to minimize ionic conductivity. The conductivity values after desiccation and subsequent drying in a vacuum at 110 °C for 1 h and at 150 °C for 4 and 15 h are presented in Table 4. As a control, the conductivity of PANI purchased from Aldrich (PANI-A) was also measured under similar conditions.

The electrical conductivity of the PVP−PANI-I was found to be about an order of magnitude higher than that of PVP−PANI-S. The higher conductivity of the PVP−PANI-I may be explained by a higher percentage of PANI present in the complex. Corroborative evidence is also provided by the higher elemental N:P ratio for

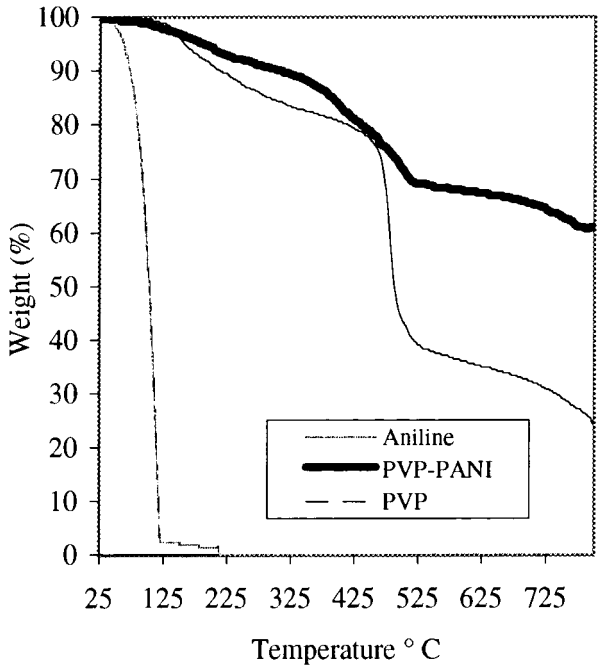

Figure 6. TGA curves of aniline, PVP, and PVP−PANI-I.

the PVP−PANI-I obtained from the elemental analysis. The conductivities of these complexes are higher than those reported for the PAA/PANI blends and PANI synthesized from N-substituted anilines.[30,31] The conductivity values are also higher than or similar to the conductivity values reported for chemically synthesized PVP−PANI. Moreover, after exposing the samples to heat under vacuum and subsequent cooling, the loss in conductivity was very minimal. This confirms that the dopant (PVP) remains complexed to PANI even after heating at 150 °C for 15 h.

Thermal Analysis of PVP−PANI-I. The TGA thermograms of aniline, PVP, and PVP−PANI-I are shown in Figure 6. The initial 6% weight loss in PVP−PANI-I and PVP until 150 °C is attributed to the loss of water. For the case of PVP, we notice a gradual weight loss in the range of 135−450 °C, and this has been attributed to the condensation of phosphonic groups activated by water loss.[32] Weight loss due to degradation starts at around 450 °C. Almost 50% of the sample by weight is lost before 520 °C. PVP−PANI-I shows a similar degradation pattern until 450 °C but becomes much less pronounced at higher temperatures. Degradation of the PVP polymer backbone seems to occur after 450 °C and up to 530 °C. However, more than 60% of the weight is retained even at 800 °C. Chemically synthesized PVP−PANI complexes are known to have poor thermal stability, and nearly 80% weight loss is observed before 625 °C.[26] The TGA curves of HCl doped polyaniline as reported[33] earlier exhibit approximately 5% weight loss at around 200 °C, indicating loss of HCl and traces of water. The weight loss, caused by thermal degradation, begins around 300 °C, and close to 45% loss of weight occurs before a temperature of 575 °C is reached. The improved conductivity/stability of the enzymatically synthesized PVP−PANI as compared with the chemically synthesized PVP−PANI reported earlier[26] may be attributed to the higher pH conditions employed in the synthesis, which promote the solubility of PVP, which in turn leads to the improved formation of the PVP−PANI electrostatic complex. Further evidence is provided by the conductivity measurements obtained after

exposure of the complex to elevated temperature. There is no observable loss of conductivity in enzymatically synthesized PVP−PANI, indicating stronger complexation of the polyelectrolyte dopant with the polyaniline.

Conclusion

The enzymatic synthesis of a conducting macromolecular complex of PVP−PANI is presented. The polymerization was accomplished in an aqueous buffer at pH 4, and the electroactive PVP−PANI complex was characterized using spectroscopy and thermogravimetry. The results indicate that appropriate control on the polymerization can be used to tune the water solubility and conductivity of the PVP−PANI molecular complex. There is also evidence for the existence of a constant ratio between the phosphonic acid repeat unit and the aniline repeat unit (1.5 to 1) in the complex prior to precipitation when there is excess PVP in the system. The enzymatically synthesized complex has improved thermal stability as compared to the chemically synthesized complex. This template-guided enzymatic approach can be extended to other organic phosphates/phosphonic acids and biologically derived polyelectrolytes. The selection of PVP as the polyelectrolyte for the polymerization of aniline has been used as the preliminary step toward extension of this concept to other biological polyelectrolytes, such as DNA, for possible applications in signal transduction and biofunctional optoelectronics.

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