

Synthesis of Conducting Water-Soluble Polyaniline with Iron(III) Porphyrin

M. R. Nabid,¹ R. Sedghi,¹ P. R. Jamaat,¹ N. Safari,¹ A. A. Entezami²

¹Department of Chemistry, Faculty of Science, Shahid Beheshti University, 1983963113, Tehran, Iran

²Faculty of Chemistry, Tabriz University, 51664, Tabriz, Iran

Received 13 September 2005; accepted 21 December 2005

DOI 10.1002/app.24034

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The porphyrin-catalyzed, template-guided polymerization of aniline was carried out in an aqueous buffer solution. Hydrogen peroxide and iron(III) tetrasulfonated tetraphenyl porphyrin catalyzed the polymerization of aniline in the presence of sulfonated polystyrene as a template. The polymerization was carried out at different pHs ranging from 1 to 5. Ultraviolet–visible spectroscopy indicated the formation of a conducting form of polyaniline. The extent of the polymerization increased with decreasing

pH of the solution. The maximum absorbance of the polaron band at 750 nm was obtained at pH 2, but when the polymerization was performed with pH 4, this band shifted to a longer wavelength. These results confirmed that a longer chain length of polyaniline was obtained with pH 4.
© 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2929–2934, 2006

Key words: polyanionic template; polyaniline; sulfonated polystyrene

INTRODUCTION

Polyaniline (PANI) is one of the most interesting conducting polymers because of its stability and good electrical and optical properties.¹ Potential applications of PANI include lightweight organic batteries,² microelectronics,³ optical displays,⁴ chemical sensors,⁵ and electromagnetic shielding.⁶ It is anticipated that the preparation of PANI will receive and more attention because of its widespread applications. Conducting PANI is synthesized chemically⁷ or electrochemically⁸ in acidic solutions. Alternative methods have been designed to improve the properties of the synthesized polymers.

The development of new efficient catalysts has an important role in polymer research. A separate activity that has been studied in recent years is the use of isolated enzymes.⁹ Enzymatic catalysis is involved in both *in vivo* and *in vitro* polymerization.¹⁰ Various synthetic polymers have been synthesized under milder conditions by enzyme-catalyzed polymerizations.¹¹ Enzymatic polymerization has been explored as an alternative approach to the synthesis of electronically and optically active polymers. The polymerization of phenolic compounds with horseradish peroxidase (HRP) as the catalyst has been reported.¹² Aniline and its derivatives have also been shown to polymerize via an enzymatic oxidation process.¹³ Recently, we reported the enzymatic synthesis of water-soluble, conducting poly(*o*-to-

luidine), poly(pyrrole), and poly(*N*-alkyl anilines).^{14–16} The reaction of aniline derivatives with hydrogen peroxide catalyzed by oxidoreductase is a route to the synthesis of industrially important polyaromatics.

HRP and related enzymes show low stability under nonphysiological conditions, and they are relatively expensive, whereas metalloporphyrins are more stable, cheaper, and more promising for industrial applications. Extensive studies have been carried out with metalloporphyrins as models of oxygenases for the oxidation of organic compounds.^{17–21} However, the polymerization of organic compounds with metalloporphyrins instead of related enzymes has received little attention.²²

Water-soluble metalloporphyrins mimic the various reactions of HRP and other monooxygenases in different reactions. In this work, we report a novel route for the polymerization of aniline with hydrogen peroxide catalyzed by anionic, water-soluble iron(III) tetra(*p*-sulfonatophenyl)porphyrin (Fe^{III}TPPS). The polymerization was carried out under different pH conditions ranging from 1 to 5 in the presence of sulfonated polystyrene (SPS) as a template. The synthesized polymer was a water-soluble, electroactive, and conducting PANI/SPS complex. The progress of the reactions was monitored spectroscopically.

EXPERIMENTAL

Poly(sodium 4-styrene sulfonated) (molecular weight = 70,000) was purchased from Aldrich Chemical Co. (Milwaukee, WI) and was used without any further purification. Hydrogen peroxide (30 wt %), aniline,

Correspondence to: M. R. Nabid (m-nabid@sbu.ac.ir).

cation-exchange resin Dowex 50W-X₈ (50-100-mesh), and all other reagents were obtained from Merck (Whitehouse Station, NJ). Aniline was purified by vacuum distillation in the presence of Zn powder before use. Fe^{III}TPPS was prepared in our laboratory through the synthesis of tetraphenylporphyrin and then the sulfonation of the compound.

Catalyst synthesis

Sodium tetra(*p*-sulfonatophenyl) porphyrin (H₂TPPS)

Pure tetraphenylporphyrin (TPP) (2 g) was synthesized according to the procedure of Adler and Long.²³ The sulfonation of TPP was performed with the Fleischer method as follows.²⁴ TPP (2 g) and concentrated H₂SO₄ (50 mL) were mixed. The mixture was heated on a steam bath for 4–5 h and then allowed to stand at room temperature for 48 h. The crude product was purified according to the procedure of Tsutsui²⁵ to yield 60% pure H₂TPPS. The purity of H₂TPPS was confirmed by ultraviolet–visible (UV–vis) and IR spectroscopy.^{26,27} The UV–vis spectrum of H₂TPPS (H₂O, pH 10) showed five peaks at 411 (soret), 515, 552, 580, and 633 nm. The IR spectrum of H₂TPPS (KBr) showed four strong bands at 1218, 1188, 1125, and 1039 cm⁻¹ due to sulfonic acid.

Sodium tetra(*p*-sulfonatophenyl) porphyrinate iron(III)

A fourfold excess of FeSO₄ was added to hot and especially neutral solutions of H₂TPPS according to the procedure of Fleischer et al.²⁴ The solution was heated on a steam bath for at least 30 min, and the pH was controlled and kept fixed at 7. Then, the pH was reduced to 3, and the solution was passed through the H⁺ form of the cation-exchange resin Dowex 50W-X₈ (50–100-mesh) to remove excess Fe³⁺; then, it was immediately neutralized. Further purification was accomplished by the precipitation of Fe^{III}TPPS from a pH 5 solution by

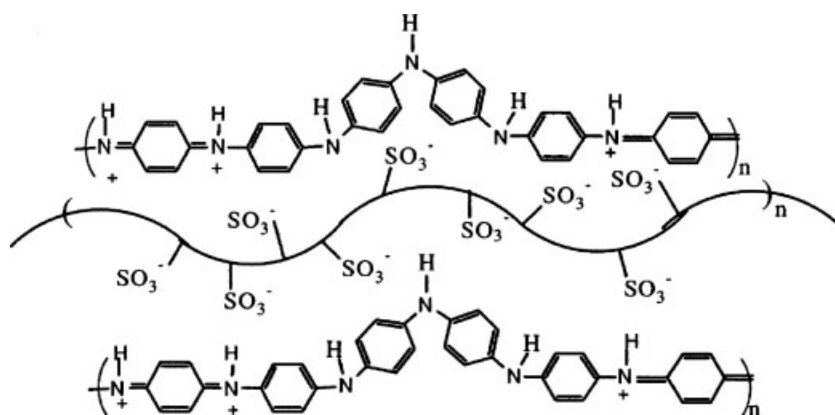
the addition of four volumes of acetone. The precipitate was redissolved in methanol and reprecipitated with acetone. The UV–vis spectrum of Fe^{III}TPPS (H₂O, pH 3) showed three peaks at 392, 528, and 680 nm. The IR spectrum of Fe^{III}TPPS (KBr) showed five strong bands at 1220, 1187, 1120, 1035, and 995 cm⁻¹.

Polymerization

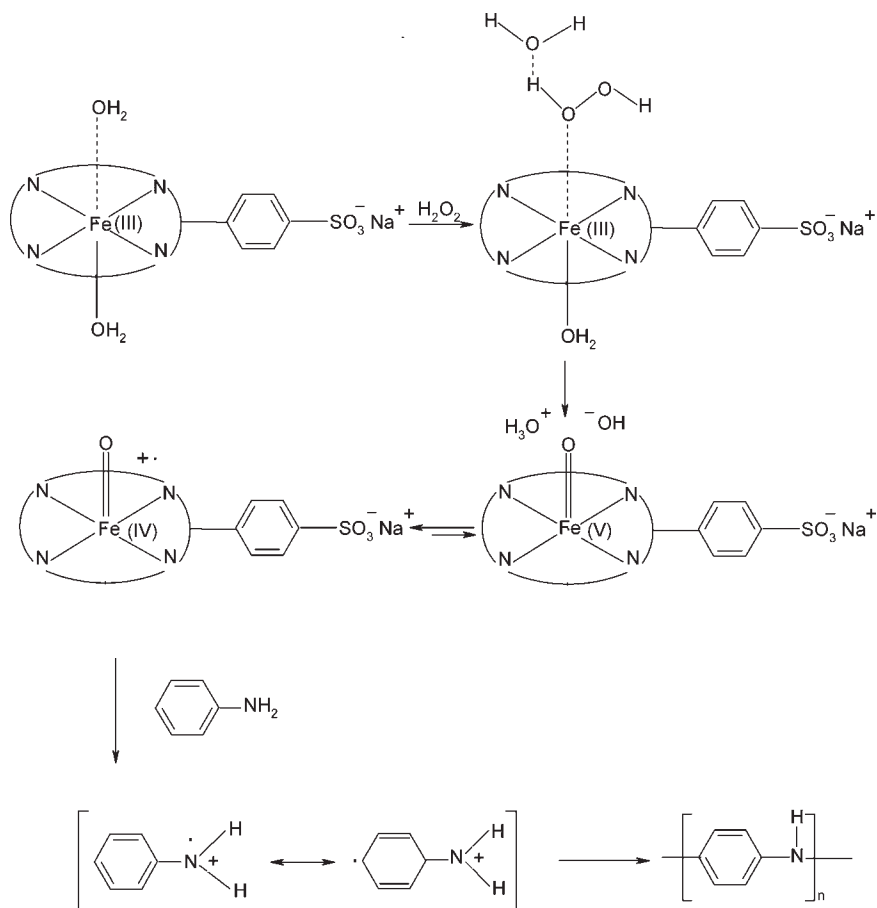
The polymerization of aniline with hydrogen peroxide catalyzed by water-soluble iron(III) tetrasulfonated porphyrin was carried out at pH values ranging from 1 to 5 at the ambient temperature. To 15 mL of a 0.2 M phosphate citric acid buffer solution were added 0.0186 g (0.09 mmol) of SPS (based on the molecular repeat unit) and 8 μL (0.09 mmol) of aniline under constant stirring. Then, the catalytic amount of the iron (III) tetra(*p*-sulfonatophenyl)porphyrin (Fe^{III}TPPS) was added (3 × 10⁻⁶ mmol). The reaction was initiated by the addition of 4.5 mL (0.02M) of diluted hydrogen peroxide under vigorous stirring. The polymerization was completed after 24 h. The final solution was dialyzed (molecular cutoff = 3000) overnight to remove any unreacted monomers and oligomers. A homogeneous, dark green, water-soluble PANI was obtained.

Characterization

UV–vis spectra were obtained with a Shimadzu UV-2100 spectrophotometer. The Fourier transform infrared (FTIR) spectrum was measured on a Bruker IFS 66/S FTIR spectrometer in the form of a dried PANI/SPS complex with KBr pellets. The cyclic voltammetry (CV) measurements were performed with a three-electrode cell with platinum as the auxiliary electrode, Ag/AgCl as the reference electrode, and Pt foil (1-cm² surface area) as the working electrode. The cyclic voltammograms were obtained in a 1.0M HCl electrolyte in polymer solutions and were scanned between – 0.2 and 1 V at scanning rates between 20 and 200 mV/s.



Scheme 1 Proposed scheme for the formation of the PANI/SPS complex.



Scheme 2 Proposed mechanism for the polymerization of aniline with FeTPPS.

RESULTS AND DISCUSSION

The peroxidase-catalyzed polymerization of aromatic amines has been extensively studied in recent years.^{28,29} A scheme of PANI synthesized in the presence of SPS is shown in Scheme 1, where SPS acts as the template and the polymerization is catalyzed with HRP. The polyelectrolyte (1) provides a preferential local environment that facilitates the para-directed coupling of the monomer, (2) provides counterions for doping, and (3) maintains the water solubility for synthesized PANI. Although HRP is a good biocatalytic approach to the synthesis of PANI, there exists a need to develop a cost-effective and newer synthetic catalyst alternative for peroxidase in these reactions. Possible applications of metalloporphyrins in catalysis have been the subject of intense research over the past few decades.³⁰ They have been used with a variety of oxidants, including hydrogen peroxide, hydroperoxides, and peracids.^{31,32} Recently, poly(ethylene glycol) modified hematin was reported as a cost-effective catalyst.³³ Also, hemoglobin was used as a biocatalyst for the synthesis of PANI in the presence of a template.³⁴

We used water-soluble iron(III) tetrasulfonated porphyrin as a synthetic catalyst for the polymerization of

aniline. The proposed mechanism for the formation of a reactive intermediate in the polymerization of aniline with FeTPPS is shown in Scheme 2. On the basis of the literature reports,^{35,36} the oxoiron(IV) radical cation is responsible for initiating the formation of the aniline cation radical, which attacks the other aniline molecule to form a dimer, and hence the reaction further propagates to give PANI.

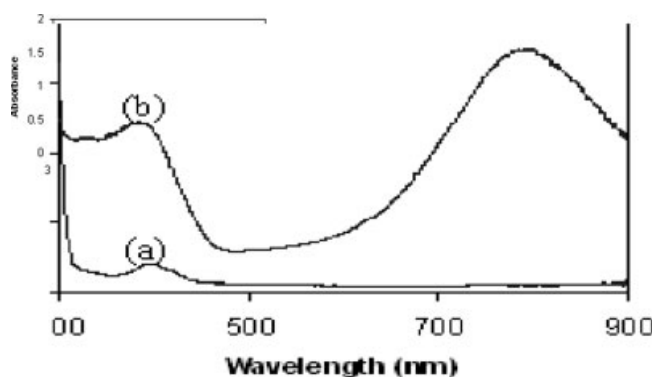


Figure 1 UV-vis spectra of the reaction mixture (a) before and (b) after the addition of H_2O_2 .

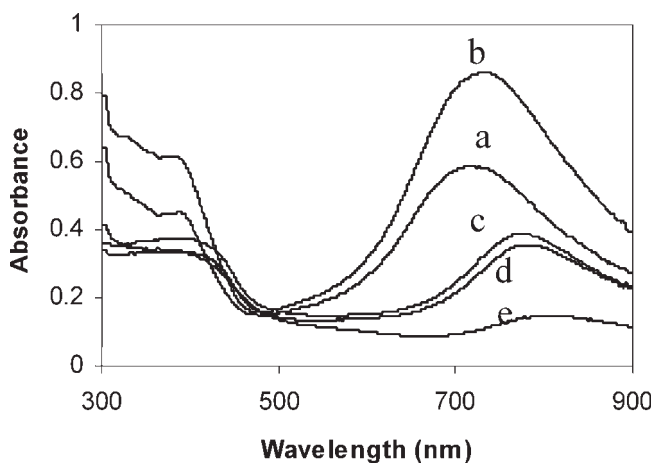


Figure 2 UV-vis spectra of the PANI/SPS complex obtained with the FeTPPS catalyst at different pHs: (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5.

Figure 1 shows UV-vis spectra of the monomer, template, and FeTPPS catalyst in the 0.1M buffer solutions at pH 4 before [Fig. 1(a)] and after [Fig. 1(b)] the addition of hydrogen peroxide. The reaction was carried out in the presence of SPS as a template, and a water-soluble conducting PANI/SPS complex was obtained. As can be seen in Figure 1(b), the characteristic peaks at 400 and 780 nm were assigned to polaron bands and confirmed the presence of a conductive form of PANI. Because SPS contained an electron-withdrawing sulfonic group in the complex, the polaron band appeared below 800 nm.

The polymerization of aniline is strongly pH-dependent. To determine the role of pH during the polymerization, the reaction was carried out under different pH conditions ranging from 1 to 5. Figure 2 shows the UV-vis spectra of PANI prepared at different pHs. The intensity of the polaron band at about 700–800 nm first increased with increasing pH of the reaction; then,

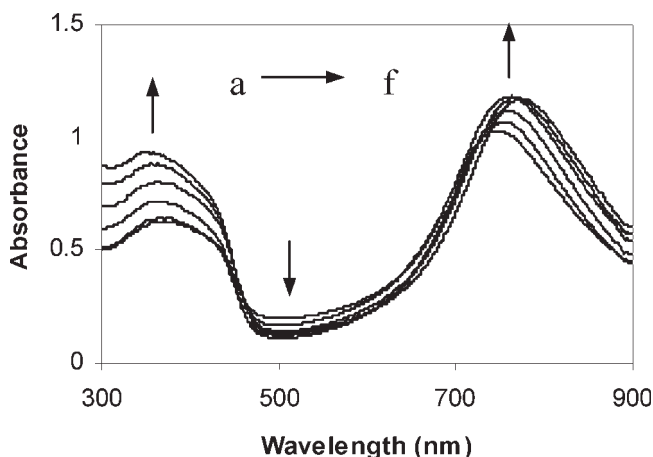


Figure 3 UV-vis spectra of the PANI/SPS complex prepared with different reaction times: (a) 4 h, (b) 8 h, (c) 12 h, (d) 1 day, (e) 2 days, and (f) 3 days.

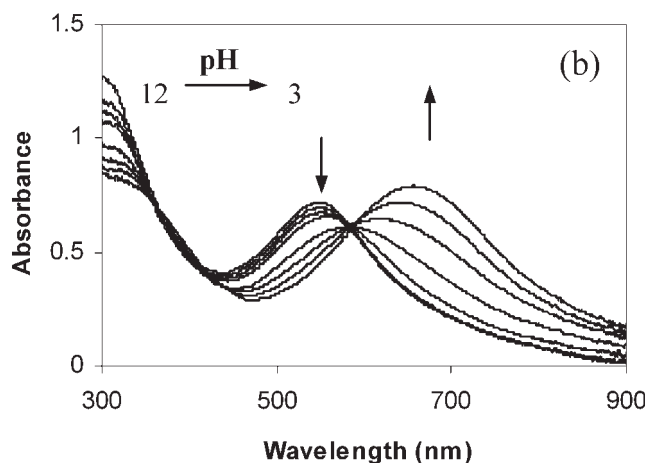
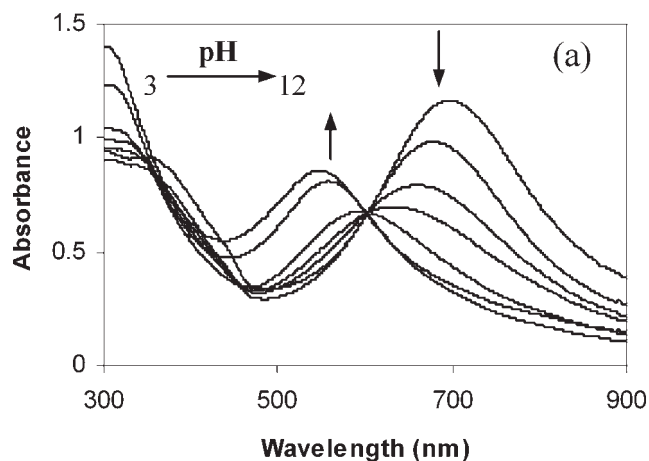


Figure 4 UV-vis spectra of PANI/SPS during dedoping and redoping with a base and an acid in the pH ranges of (a) 3–12 and (b) 12–3.

with the pH increasing more, it decreased. The maximum absorbance was obtained at pH 2 under the same conditions. However, because acid solutions of FeTPPS

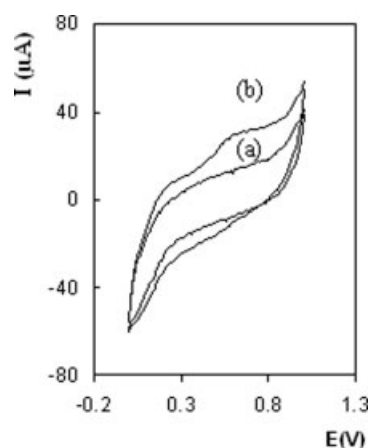


Figure 5 Cyclic voltammograms of (a) a blank solution and (b) the PANI/SPS complex in 1.0M HCl at a scanning rate of 100 mV/s. I, current; E, potential.

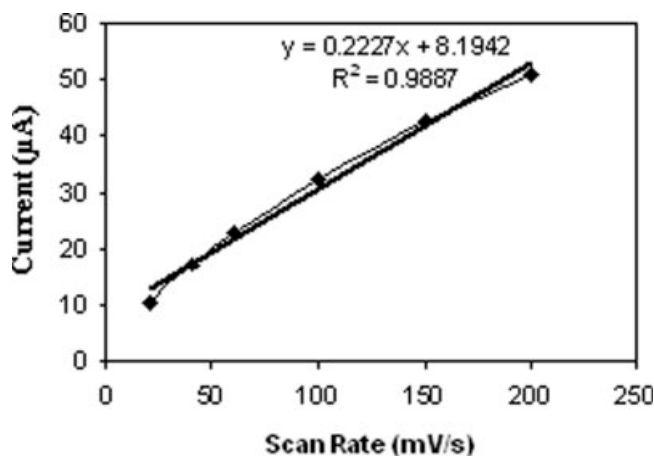


Figure 6 Plot of the anodic peak current versus the scanning rate for the PANI/SPS complex.

slowly degenerated to Fe^{3+} and the porphyrin diacid, it seems that under a strongly acidic solution, Fe^{3+} competed with FeTPPS in the polymerization of aniline catalyzed by hydrogen peroxide. On the other hand, as the pH of the solution increased, the polaron band became broader and shifted to longer wavelengths. Because the absorption of the polaron band was strongly dependent on the molecular weight of the polymer,³⁷ this indicated the difference in the molecular weight of the polymer with changes in the pH. Therefore, we preferred that the reactions be carried out in pH 4 buffer solutions because the catalyst was more stable at this pH and a longer polymer chain was obtained.

Figure 3 shows the UV-vis spectra of the PANI/SPS complex prepared with different reaction times. The peak intensity reached a maximum after 4 h, but after 1 day, the polaron band at 760 nm shifted to longer

wavelengths because of the possible formation of a polymer with a longer chain length. There was no significant change observed after 3 days.

Redox reversibility

PANI/SPS was used for studying the reversible redox behavior of the polymer in the complex. The evaluations of the absorption spectra were studied in aqueous solutions, and the results are presented in Figure 4. The polaron bands at 400 and 750 nm confirmed that the complex was in a doped state at an acidic pH. As can be seen in Figure 4(a), when the pH was increased from 2 by 1 N NaOH, the polaron bands gradually disappeared with the emergence of a new peak at 550 nm due to the exciton transition. At pH 12, PANI was fully dedoped, and the solution color changed from green to blue and finally to purple.

The dedoped form of the complex was redoped by titration with 1 N HCl. Figure 4(b) shows that these dedoping/redoping processes were reversible. The isobestic points were observed clearly. This pH-induced redox reversibility demonstrated that electroactive PANI was synthesized by this method.

Electrochemical properties

The electrochemical behavior of the PANI/SPS complex was characterized with CV. Figure 5 shows the cyclic voltammograms of a blank solution containing SPS and porphyrin in a catalytic concentration and the PANI/SPS complex. The CV curves were recorded in a 1M HCl solution at a scanning rate of 100 mV/s. Only one set of redox peaks at $E_{1/2} = 0.6$ V, where $E_{1/2}$ is the half-wave potential, belonged to the complex. Similar

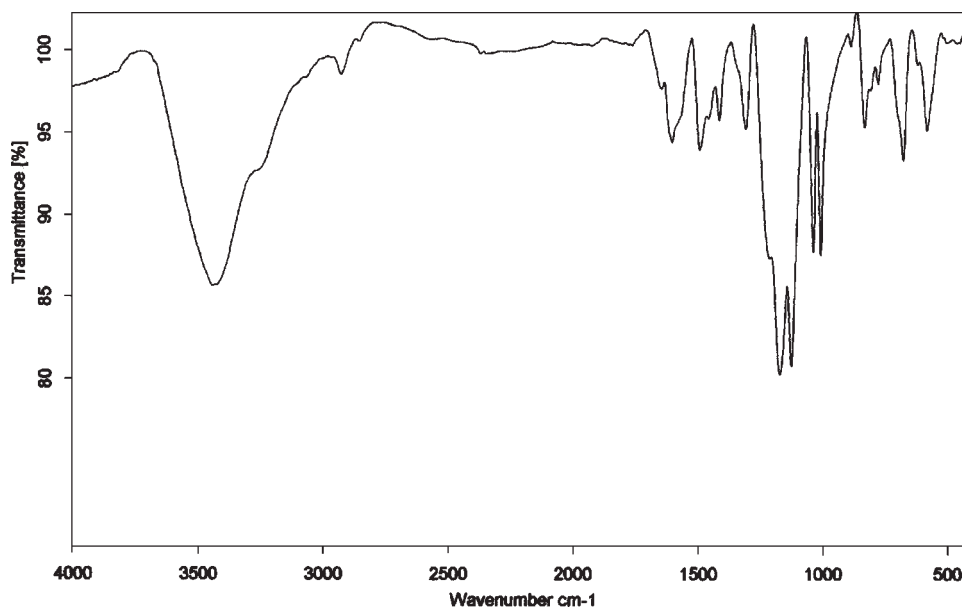


Figure 7 FTIR spectrum of the PANI/SPS complex synthesized with the FeTPPS catalyst.

results have been observed previously.²⁹ The absence of two anodic peaks probably was due to the resistance of the PANI/SPS complex to oxidation to another state.²⁵ The presence of SPS and porphyrin in the synthesized PANI influenced the electrochemical properties of the complex. The details of the effects of these compounds are still under investigation. These recorded CV curves suggested that the porphyrin-synthesized PANI was electrochemically active.

Recording the cyclic voltammograms at different scanning rates between 20 and 200 mV/s, we observed that there was an appreciable change in the cathodic and anodic peak current values. Figure 6 shows a linear relationship between the anodic peak current and the scanning rate for the PANI/SPS complex. The slope of this curve indicated the electroactivity of the polymer, and the complex showed a convenient electroactivity.

FTIR spectroscopy

FTIR spectra of the PANI/SPS complex prepared at pH 4 with porphyrin catalysts are shown in Figure 7. The bands around 1599 and 1490 cm^{-1} are due to the ring stretching of the quinoid and benzenoid forms of PANI, respectively. The band at 1305 cm^{-1} was assigned to C—N stretching of a secondary aromatic amine.³⁸ The band at 1125 cm^{-1} is due to charge delocalization on the polymer backbone.³⁹ The peak at 830 cm^{-1} , corresponding to the 1,4-disubstituted aromatic, in the PANI/SPS spectrum confirms head-to-tail PANI formation.⁴⁰ Also, the peaks observed at 1005 and 1035 cm^{-1} , corresponding to symmetric and asymmetric S=O stretching, confirm the presence of SPS in the complex.⁴¹ These results are in good agreement with spectra obtained from chemically synthesized PANI.

CONCLUSIONS

The synthesis of an electroactive PANI was accomplished with a water-soluble iron(III) tetrasulfonated porphyrin in the presence of a template. The robustness of the synthetic porphyrin catalyst was demonstrated by the ability of this catalyst to carry out the polymerization reaction at various pHs. The best results were obtained under strongly acidic conditions. Because of the slow demetallation of the catalyst under these conditions, polymerization was carried out in an aqueous phosphate buffer in a pH 4 solution. At this pH, the polaron band became broader and shifted to a longer wavelength because of the possible formation of PANI with a longer chain length. FTIR and UV-vis spectroscopy characterization showed that the obtained PANI was similar to previous polymers obtained chemically, electrochemically, or enzymatically. This process is simple (one-step), chemically mild, and environmentally benign and requires minimal separa-

tion and purification. With this method, water-soluble, conducting PANI in the presence of SPS was obtained.

References

- MacDiarmid, A. G. *Synth Met* 2002, 125, 11.
- Naoi, K.; Ogano, S.; Osaka, T. *J Electrochem Soc C* 1988, 135, 119.
- Chen, S. A.; Fang, Y. *Synth Met* 1993, 60, 215.
- Jelle, B. P.; Hagen, G. *J Electrochem Soc* 1993, 140, 3560.
- Liu, C. H.; Liao, K. T.; Huang, H. J. *Anal Chem* 2000, 72, 2925.
- Wood, A. S. *Mod Plast* 1991, 47.
- Adams, P. N.; Laughlin, P. J.; Monkman, A. P. *Synth Met* 1996, 76, 157.
- Verghese, M. M.; Ramanathan, K.; Ashraf, S. M.; Kamalasanan, M. N.; Malhotra, B. D. *Chem Mater* 1996, 8, 822.
- Karamyshev, A. V.; Shleev, S. V.; Koroleva, O. V.; Yaropolov, A. I.; Sakharov, I. Y. *Enzyme Microb Technol* 2003, 33, 556.
- Uyama, H.; Kobayashi, S. *J Mol Catal B* 2002, 19, 117.
- Gross, R. A.; Kumar, A.; Kalra, B. *Chem Rev* 2001, 101, 1097.
- Dordick, J. S.; Morletta, M. A.; Klibanov, A. M. *Biotechnol Bioeng* 1987, 30, 31.
- Ichinohe, D.; Muranaka, T.; Sasaki, T.; Kobayashi, M.; Kise, H. *J Polym Sci Part A: Polym Chem* 1998, 36, 2593.
- Nabid, M. R.; Entezami, A. A. *Eur Polym J* 2003, 39, 1169.
- Nabid, M. R.; Entezami, A. A. *J Appl Polym Sci* 2004, 94, 254.
- Nabid, M. R.; Entezami, A. A. *Polym Adv Technol* 2005, 16, 305.
- McLain, J.; Lee, J.; Groves, J. T. In *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Menier, B., Ed.; Imperial College Press: London, 2000; p 91.
- Ortiz de Montellano, P. R. *Cytochrome P-450: Structure, Mechanism and Biochemistry*, 2nd ed.; Plenum: New York, 1995; p 652.
- Newcomb, M.; Shen, R.; Choi, S.-Y.; Toy, P. H.; Hollenberg, P. F.; Vaz, A. D. N.; Coon, M. J. *J Am Chem Soc* 2000, 122, 2677.
- Nam, W.; Lim, M. H.; Oh, S.-Y. *Inorg Chem* 2000, 39, 5572.
- Khavasi, H. R.; Davarani, S. S. H.; Safari, N. *J Mol Catal A* 2002, 188, 115.
- Angrish, C.; Chauhan, S. M. S. *Arkivoc* 2004, 8, 61.
- Adler, A. D.; Long, F. R. *J Org Chem* 1967, 32, 476.
- Fleischer, E. B.; Palmer, J. M.; Srivastava, T. S.; Chatterjee, A. *J Am Chem Soc* 1971, 93, 3162.
- Tsutsui, M. *J Org Chem* 1973, 38, 2103.
- Thomas, D. W.; Martell, A. E. A. *J Am Chem Soc* 1959, 81, 5111.
- Chen, D. M.; Zhang, Y. H. *Spectrochim Acta A* 2003, 59, 87.
- Liu, W.; Kumar, J.; Tripathy, S.; Samuelson, L. *Langmuir* 2002, 18, 9696.
- Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K. J.; Samuelson, L. *J Am Chem Soc* 1999, 121, 71.
- Cunningham, I. D.; Danks, T. N.; Hay, J. N.; Hamerton, I.; Gunathilagan, S. *Tetrahedron* 2001, 57, 6847.
- Meunier, B. *Chem Rev* 1992, 92, 1411.
- Iwanejko, R.; Battioni, P.; Mansuy, D.; Mlodnicka, T. *J Mol Catal A* 1996, 111, 7.
- Roy, S.; Fortier, J. M.; Nagarajan, R.; Tripathy, S.; Kumar, J.; Samuelson, L. A.; Bruno, F. F. *Biomacromolecules* 2002, 3, 937.
- Xing, H.; Yu-Ying, Z.; Kai, T.; Guo-Lin, Z. *Synth Met* 2005, 150, 1.
- Groves, J. T.; Nemo, T. E. *J Am Chem Soc* 1983, 105, 5786.
- Groves, J. T.; Watanabe, Y. *J Am Chem Soc* 1988, 110, 8443.
- Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1989, 32, 263.
- Boyer, M. I.; Quillard, S.; Rebourt, E.; Louarn, G.; Buisson, J. P.; Monkman, A.; Lefrant, S. *J Phys Chem B* 1998, 102, 7382.
- Kim, Y. H.; Foster, C.; Chiang, J.; Heeger, A. J. *Synth Met* 1988, 26, 49.
- Chevalier, J. W.; Bergeron, J. Y.; Dao, L. H. *Macromolecules* 1992, 25, 3325.
- Chen, S. A.; Hwang, G. W. *Polymer* 1997, 38, 333.