Communications to the Editor

Biologically Derived Conducting and Water Soluble Polyaniline

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Introduction. Conducting polymers hold tremendous promise as a new class of advanced materials for numerous technological applications.[1−3] Polyaniline, an extensively investigated conducting polymer, is derived from a common, readily available monomer, is stable and redox active, and can reach metallike conductivities upon protonation.[4−7] Commercial use of polyaniline however, has been limited due to harsh synthetic conditions and poor processability, electrical stability, and environmental compatibility. Numerous self-doped methods have been recently developed to improve both the electrical stability and solubility of polyaniline.[8−11] These chemical polymerization conditions, however, remain harsh and require additional separation and purification steps before processing of the conducting polyaniline is possible.

Enzymatic polymerization of anilines has been studied as a promising environmentally friendly and more efficient synthetic alternative. Horseradish peroxidase (HRP) in the presence of hydrogen peroxide catalyzes the polymerization of phenol and aromatic amines to produce high molecular weight polymers.[12] The polymerization reaction, however, is known to be both ortho and para directed and typically results in branched polymeric materials which are intractable and have poor electrical properties. To minimize branching and facilitate processing, a large number of experimental situations have been investigated including aqueous and organic solvent mixtures,[12,13] organized reaction environments such as reversed micelles,[14] and Langmuir monolayers.[15] Most recently, enzymatic polymerization has been used to prepare water-soluble polyanilines where the monomer is simply a water soluble analogue of aniline.[16,17] The resultant polymers in all these cases are synthesized under mild conditions and offer many processing advantages. However, these materials must be converted to the conducting form by doping (protonation) under extreme acidic conditions for electrical conductivity and still remain limited in their electrical and optical properties.

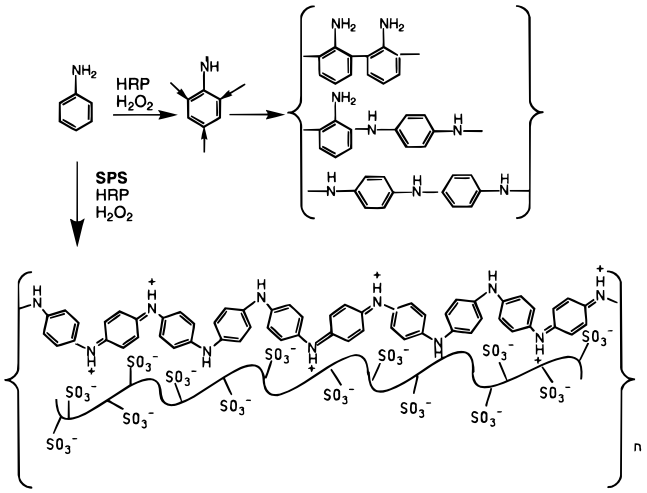

Figure 1. Branched structures of the traditional ortho−para directed enzymatic polymerization of aniline which results in an electrically inactive form of polyaniline vs enzymatic polymerization of aniline (at pH 4) in the presence of SPS. This reaction promotes a more linear, para-directed reaction and results in the conducting emeraldine salt form of polyaniline.

Recently, in a major improvement in the synthesis and doping of polyaniline, polyelectrolyte- (polyanion-) assisted chemical polymerization of aniline has been used to simultaneously form a water-soluble and doped conducting complex of polyaniline. The monomers, upon exposure to strong chemical oxidants, polymerize and complex with the polyanion, resulting in a water-soluble polyaniline in the conducting emeraldine salt form.[18−21] While the synthesis still requires strong oxidants and/or modified aniline monomers, subsequent doping and processing limitations have been minimized. The method we describe here combines the advantages of the environmentally benign and mild enzyme-catalyzed polymerization of aniline with the simultaneous doping and processability enhancements of the polyelectrolyte-assisted chemical polymerization. A simple, inexpensive, environmentally benign synthesis of a stable and processable conducting polymer has been achieved.

Experimental Section. Aniline, sulfonated polystyrene (SPS) with an M_w of 70 000, and 30% hydrogen peroxide were purchased from Aldrich Chemicals and used as received. Horseradish peroxidase (HRP) was purchased from Sigma Chemicals and used as received. The polymerization of aniline was carried out in 0.1 M sodium phosphate buffered aqueous solutions with the pH ranging from 4.0 to 10.0. In each case, aniline monomer was first dissolved in concentrations ranging from 10 to 100 mM and SPS (based on the repeat unit) was then added to the desired molar (aniline:SPS) ratio. To initiate polymerization, a catalytic amount of HRP

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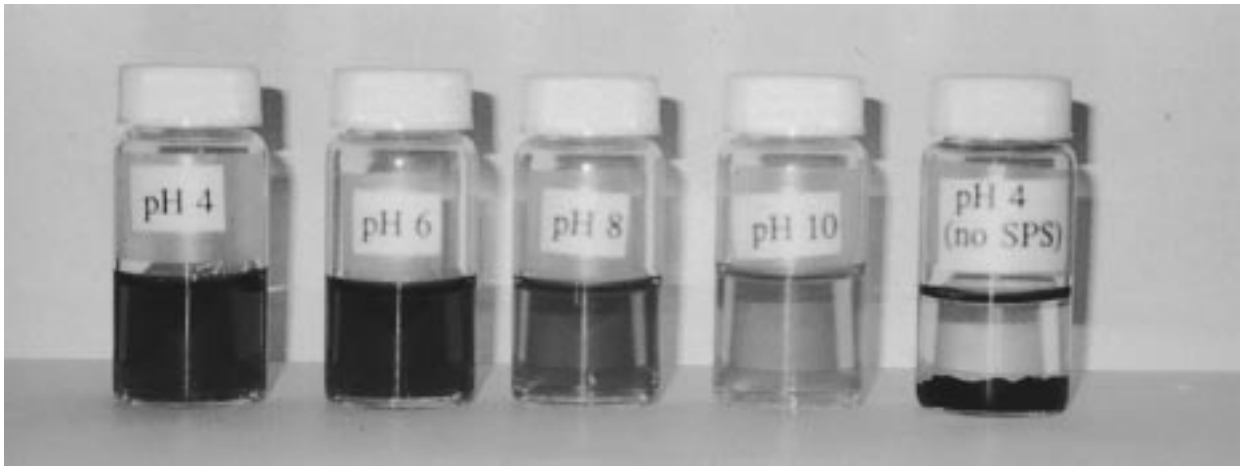

Figure 2. Photograph of a series of SPS/polyaniline (1:2 ratio) solutions prepared at pH's of 4, 6, 8, and 10, respectively, where the last vial is that of aniline polymerized at pH 4 without SPS.

was added to the solution (1−5 unit/mL) followed by addition of a stoichiometric amount of hydrogen peroxide (2:1, hydrogen peroxide to aniline monomer), in 10 μL increments, 10 min apart with constant stirring. The reactions were left to stir for approximately 3 h to bring the reaction to completion. Since only catalytic amounts of HRP are used and the hydrogen peroxide is converted to water during the reaction, minimal separation and purification steps are required. Absorption studies were recorded using a Perkin-Elmer Lambda 9 UV−vis−near-IR spectrophotometer.

Results and Discussion. In the process of carrying out an enzymatic, polyelectrolyte-assisted polymerization of aniline, remarkable, unexpected synergies are obtained. First, the polyelectrolyte acts as a template upon which the aniline monomers and/or oligomers preferentially align themselves and form a complex that leads to mostly para-directed synthesis promoting extended conjugation of the resulting polyaniline chains with limited parasitic branching. This, in itself, leads to significant improvement and control over the electronic properties of the complex and results in a conducting (redox active) form of polyaniline as shown in Figure 1. Second, the polyelectrolyte actually serves as a large molecular counterion which is integrated and essentially locked to the polyaniline chains. This polyemeraldine salt with the polyanion is extremely stable and once formed ensures stability of the desired electrical properties. Last, the polyelectrolyte template serves to provide water solubility of the final template−polyaniline complex for facile, inexpensive processing.

The pH of the reactant solution is critical in controlling the aniline monomer−polyanion complex formation and hence the electrical activity of the resulting polyaniline backbone. As shown in Figure 2, solutions ranging in color from green (at low pH) to blue (near neutral pH) and finally to yellow (at high pH) are obtained. These colors and the corresponding absorption spectra (not shown) correspond to the well-known oxidation states of chemically prepared polyaniline.[22,23] Of particular interest is the green solution which was prepared at pH 4 (higher than that required for chemical synthesis of polyaniline). Visible absorption studies show that this solution has an absorption maximum at approximately 750 nm, indicating the formation of the conducting, emeraldine salt form of polyaniline. However, as the pH of the reactant solutions is increased, the absorption maximum of the resultant polymer shifts

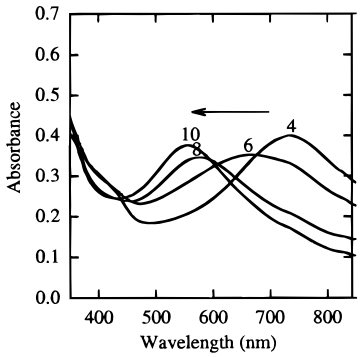

Figure 3. Visible absorption of the SPS/aniline (1:2 ratio) complex, prepared at pH 4, with increasing pH.

to shorter wavelengths. This corresponds to more parasitic branching (ortho coupling) and the less protonated forms of polyaniline.[24,25] These changes may be explained by weaker electrostatic adsorption and/or poorer organization of the aniline monomer along the anionic sulfonate groups of the polyelectrolyte template under higher pH conditions. Since the pK_a of aniline is 4.60, a pH of 4 is sufficient to provide the necessary cationic charges which promote preferential alignment and salt formation with the polyanion. In all cases, no precipitation of the polymer complex was observed from any of the solutions which contained the SPS polyelectrolyte. If the polymerization is carried out in the absence of SPS however, a brown, murky solution immediately forms followed by precipitation of uncomplexed, low molecular weight polyaniline.

The reduction/oxidation reversibility of the SPS/PAN complex is demonstrated in Figure 3. A peak at 750 nm is observed for the initial SPS/PAN complex formed at pH 4. As the pH is adjusted to 6, 8, and finally 10 the absorption peaks are observed to shift to much shorter wavelengths, which correspond to changes in the protonation of the polyaniline backbone. The reverse behavior is observed as the pH is sequentially adjusted back to 4.0. This complete redox reversibility further confirms that the polyaniline formed under these conditions is the electrically active form. Redox reversibility is not observed for SPS/PAN complexes formed at pH 7 or higher, however, as these complexes show little or no change in absorption with pH. This may be explained by weaker electrostatic interaction of the aniline and the polyelectrolyte instead of more direct integration with the polyelectrolyte counterion sites.

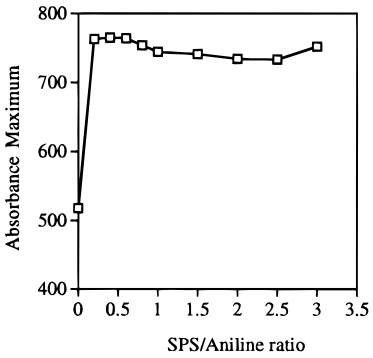

Figure 4. Plot of absorbance vs ratio of SPS:aniline.

Subsequently, a more ortho-directed synthesis prevails, leaving behind a more highly branched and less intimately connected, insulating form of polyaniline.

Optimization of the ratio of SPS to aniline was carried out by polymerizing with varying ratios of 1:10 to 10:1 for SPS to aniline at pH 4.0. Figure 4 shows a plot of the absorption peak vs the ratio of SPS:aniline. It is apparent from these results that a ratio of 1:2 (SPS/aniline) is the minimum amount needed to obtain the conducting form of polyaniline, which has its signature peak at 750 nm. This ratio is also close to the minimum amount of SPS needed to maintain complete water solubility of the final complex, and it corresponds to roughly one sulfonate (counterion) group per two aniline monomers. As the amount of SPS is increased, the absorption remains at 750 nm, suggesting that maximum counterion levels and integration of the SPS to the polyaniline have been achieved. Four-point probe conductivity measurements carried out on dried films of the 1:2 (SPS/PAN) system prepared at pH 4 were found to be as high as 10^{-1} S/cm. As the ratio of SPS in the complex was increased, however, the conductivities were found to decrease to as low as 10^{-6} S/cm, suggesting that the insulating nature of the SPS is contributing significantly to the bulk electrical properties of the assembly. Infrared spectroscopy, XPS, and elemental analysis data are consistent with the proposed conducting form of polyaniline. This complex, to date, has also demonstrated good electrical and solution stability as no decrease in conductivity of the cast films or precipitation of polymer from solution has been observed after 6 months of storage at room temperature.

This new biological route to the synthesis of a water-soluble, truly conducting form of polyaniline is particularly attractive as it now allows for a completely benign, one-pot synthesis where the desired final product requires little or no further purification. The process is general; numerous anilinofunctional comonomers may be employed to produce important electroactive copolymers. Also, a template with a specific structure, shape, and size may be incorporated to fabricate desirable architectures for a host of electronic and optical applications. In this first report of an optimized biochemical reaction using complexed monomers on a polyelectrolyte template, an approach to biochemical synthesis of a conducting polymer has been established.

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References and Notes

(1) Reynolds, J. R. *CHEMTECH* **1988**, July, 440−447.
(2) Barisci, J. N.; Conn, C.; Wallace, G. G. *TBIP* **1996**, *4* (9), 307−311.
(3) Angelopoulos, M. In *The Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T.; Elsenbaumer, R., Reynolds, Eds.; Marcel Dekker: New York, 1997; pp 921−944.
(4) Chiang, J. C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.
(5) Cao, Y.; Li, S.; Xue, Z.; Guo, D. *Synth. Met.* **1986**, *16*, 305.
(6) Epstein, A. J.; Ginder, J. M.; Zuo, F.; Woo, H. S.; Tanner, D. B.; Richter, A. F.; Angelopoulos, M.; Huang, W. S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *21*, 63−70.
(7) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss.; Chem. Soc.* **1989**, *88*, 317.
(8) Wei, X.-L.; Wang, Y. Z.; Long, S. M.; Bobeczko, C.; Epstein, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 2545−2555.
(9) Nguyen, M. T.; Kasai, P.; Miller, J. L.; Diaz, A. F. *Macromolecules* **1994**, *27*, 3625−3631.
(10) Chan, H. S. O.; Ho, P. K. H.; Ng, S. C.; Tan, B. T. G.; Tan, K. L. *J. Am. Chem. Soc.* **1995**, *117*, 8517−8523.
(11) Chen, S.-A.; Hwang, G.-W. *J. Am. Chem. Soc.* **1995**, *117*, 10055−10062.
(12) Akkara, J. A.; Senecal, K. J.; Kaplan, D. L. *J. Polym. Sci.; Polym. Chem.* **1991**, *29*, 1591−1574.
(13) Ikeda, R.; Uyama, H.; Kobayashi, S. *Macromolecules* **1996**, *29*, 3053−3054.
(14) Akkara, J. A.; Ayyagari, M.; Bruno, F.; Samuelson, L.; John, V. T.; Karayigitoglu, C.; Tripathy, S.; Marx, K. A.; Rao, D. V. G. L. N.; Kaplan, D. L. *Biomimetics* **1994**, *2* (4), 331−339.
(15) Bruno, F. F.; Akkara, J. A.; Samuelson, L. A.; Kaplan, D. L.; Mandal, B. K.; Marx, K. A.; Kumar, J.; Tripathy, S. K. *Langmuir* **1995**, *11*, 889−892.
(16) Alva, K. S.; Marx, K. A.; Kumar, J.; Tripathy, S. K. *Macromol. Rapid Commun.* **1996**, *17*, 859−863.
(17) Alva, K. S.; Kumar, J.; Marx, K. A.; Tripathy, S. K. *Macromolecules* **1997**, *30*, 4024−4029.
(18) Liu, J.-M.; Sun, L.; Hwang, J.-H.; Yang, S. C. *Mater. Res. Soc. Symp. Proc.* **1992**, *247*, 601−606.
(19) Sun, L.; Yang, S. C.; Liu, J.-M. *Polym. Prepr.* **1992**, *33* (2), 379−380.
(20) Angelopoulos, M.; Patel, N.; Shaw, J. M.; Labianca, N. C.; Rishton, S. A. *J. Vac. Sci. Technol.* **1993**, *B11*, 2794−2797.
(21) Sun, L.; Liu, H.; Clark, R.; Yang, S. C. *Synth. Met.* **1997**, *84*, 67−68.
(22) Epstein, A. J.; Ginder, J.-M.; Zuo, F.; Bigelow, R. W.; Woo, H.-S.; Tanner, D. B.; Richter, A. F.; Huang, W. S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *18*, 303−309.
(23) MacDiarmid, A. G.; Chiang, J.-C.; Richter, A. F.; and Epstein, A. J. *Synth. Met.* **1987**, *18*, 285.
(24) Bloor, D.; Monkman, A. *Synth. Met.* **1987**, *21*, 175−179.
(25) Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc.; Faraday Trans 1* **1986**, *82*, 2385−2400.

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