Article

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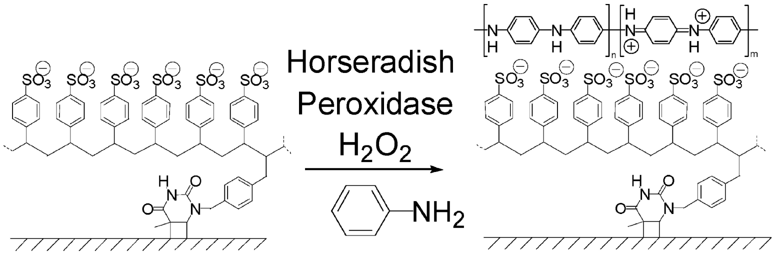
J. Am. Chem. Soc., **2005**, 127 (25), 9100-9104• DOI: 10.1021/ja042438v • Publication Date (Web): 07 June 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Published on Web 06/07/2005

Photo-cross-linked Immobilization of Polyelectrolytes for Enzymatic Construction of Conductive Nanocomposites

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Abstract: Horseradish peroxidase has been demonstrated to catalyze the oxidative polymerization of aniline to form conductive polyaniline. This process is facilitated by the presence of a macromolecular template with sulfonic acid groups that provide a unique environment for the formation of the conducting polymer. Here we report the use of a photo-cross-linkable thymine-based polymer with phenylsulfonate groups as a templating substrate. This allows for an aqueous-based environmentally benign photopatterning of a conductive material. A description and results of this process are presented.

Introduction

Surface patterning with conjugated polymers has received quite a bit of attention recently due to their potential applications in a variety of microelectronic and electrooptical devices.[1] The electrical properties of conjugated polymers can be manipulated by controlling the method of preparation[2] or by the addition of secondary materials (dopants)[3] that effect electron transport. The prospect of being able to precisely tailor the physical and electrical properties of conjugated polymers makes them attractive potential alternatives for both metals and semiconductors in various applications. The techniques that are typically used to achieve surface patterning with conjugated polymers can be divided into three broad categories: (1) coating a surface with a layer of conjugated polymer and patterning the surface by selectively removing the film from selected areas;[4] (2) patterning a surface with a material that serves as a template for subsequent polymerization when exposed to a monomer solution;[5] and (3) polymerization in solution where the conjugated polymer subsequently precipitates on the prepatterned substrate.[6]

One of the obstacles that prevents the wide utilization of conjugated polymers is the harsh conditions that are used for the polymerizations. Typical procedures employ highly acidic conditions (usually $pH < 1$). To avoid the environmental damage and reduce the associated manufacturing costs, enzymatic polymerization pathways have been explored.[7] However it was found that in aqueous media, enzymatic polymerization of aromatic molecules leads to the formation of low molecular weight oligomers that precipitate out easily.[8] When organic solvents were added to the aqueous buffer in order to improve polymer solubility, high molecular weight polymers were successfully obtained.[9−13] Furthermore it was demonstrated that by varying the composition of the solvent−water mixture it is possible to control the structural properties of the enzymatically synthesized polymers.[14] However there are some drawbacks of this approach. It requires the use of organic solvents that are not environmentally benign and are derived from petroleum feedstocks, and also enzyme catalysis works better in aqueous media. Further, in the absence of water-soluble polyelectrolytes, branched polymeric chains of the conjugated polymers are formed, and this significantly lowers the conductivity.[10,11] An alternative technique has been developed where conjugated

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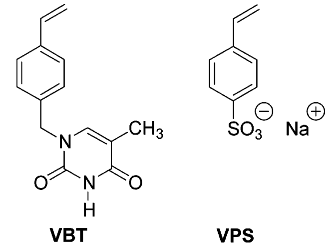
Scheme 1. Chemical Structures of VBT and VPS Monomers



polymers based on aniline, phenol, and their derivatives are enzymatically synthesized with horseradish peroxidase (HRP) in aqueous media, under mild conditions and in the presence of polyelectrolytes.[15−20] This method is an excellent example of Green Chemistry.[21]

For this process to generate useful conductive materials, a suitable acidic template must be provided in order to align aniline monomers into the growing polymer chains. Any system that provides an appropriate geometry and charge distribution can function as an acidic template for this polymerization. Sulfonated polystyrene (SPS) was first used as a template for polymerization in aqueous solution.[15,16] Since then, a wide range of templates have been used,[22] and even the phosphate groups of DNA have proven to be a suitable template for this approach.[18] Our interests in green chemistry,[23] coupled with our work with thymine-based photoresist systems,[24] have allowed us to devise a process to pattern various surfaces with sulfonated polystyrene comonomer derivatives containing vinylbenzylthymine (VBT) and vinylphenylsufonate (VPS).[25] The structures of VBT and VPS are presented in Scheme 1.

Typical VBT:VPS monomer ratios ranging from 1:1 through 1:32 have been synthesized and coated on hydrophilic substrates. These environmentally benign, water-soluble photopolymers undergo a $2\pi + 2\pi$ photodimerization reaction of the pendant thymine units when exposed to low levels of ultraviolet irradiation.[26] The photodimers create cross-linked networks in regions of ultraviolet exposure, rendering the polymer significantly less water soluble (virtually insoluble) in those areas. This process leads to an immobilization of the physisorbed polymer in response to the irradiation (hence a photoresist), allowing removal of the unexposed regions by a simple aqueous wash. (The unreacted photopolymeric material can be recovered and reused in subsequent applications.) With this novel expertise to specifically pattern sulfonated polystyrene derivatives on various substrates in hand we set out to explore the ability of these patterned surfaces to function as a template for the HRP-catalyzed polymerization of aniline under mild conditions.

This report describes the successful use of photo-cross-linkable VBT−VPS copolymers as a template for HRP-prepared conductive polyaniline polymers (Pani). VBT−VPS copolymers, both in aqueous solution and when immobilized on a surface as a result of photo-cross-linking, provide a suitable template for the enzymatic synthesis of Pani. Also, it is demonstrated that water-soluble Pani/VBT−VPS complexes can be adsorbed onto preformed VBT−VPS surface patterns. The detailed characterization and behavior of these materials are presented.

Results and Discussion

This paper describes the strategy to utilize the properties of both functionalities present in VBT−VPS copolymer. The sulfonate groups in VPS coordinate and align aniline monomers for subsequent polymerization into conductive Pani, similar to Pani/SPS, while thymine pendant groups in VBT are used for UV-induced cross-linking, allowing surface patterning with conductive Pani. This strategy is presented in Scheme 2.

The goal of the study is to show that on one hand the VBT−VPS provides a viable template for conductive Pani synthesis and on the other hand to demonstrate that using VBT−VPS as a template for Pani synthesis allows for surface patterning with conductive Pani. The important concern that this study is intended to address is that the presence of VBT comonomers in VBT−VPS polymer might be disrupting the continuous VPS chains, which could result in significant decrease of the Pani average chain length, which can negatively affect Pani conductivity. Another possible concern is that the cross-linked VBT−VPS polymer, immobilized on the surface, has more rigid structure and more tightly coiled chains than does SPS in aqueous solution, which could result in decreased ability of the VPS to coordinate and align aniline monomers, making it a less suitable Pani polymerization template.

Therefore incorporation of VBT comonomers into SPS, resulting in VBT−VPS, may have a double effect, on one hand providing a mechanism for highly desirable environmentally benign surface patterning with conductive Pani, but on the other hand decreasing Pani conductivity. The attractiveness of the above tradeoff will be defined by whether the Pani obtained by the proposed method still belongs to the class of conductive polymers.

VBT−VPS as Template. To compare the reversible redox behavior of Pani that was polymerized on an SPS template to the redox behavior of Pani that was polymerized on our photo-cross-linkable VBT−VPS template, the UV−vis absorption spectra of Pani/VBT−VBS aqueous solution were monitored as a function of pH via titration with 1 M NaOH (Figure 1A) and 1 M HCl (Figure 1B). The behavior of the Pani/SPS complex under the same conditions is described in detail in the previous study.[16] At low pH the Pani/VBT−VPS solution is green and its spectrum features the characteristic peaks at about

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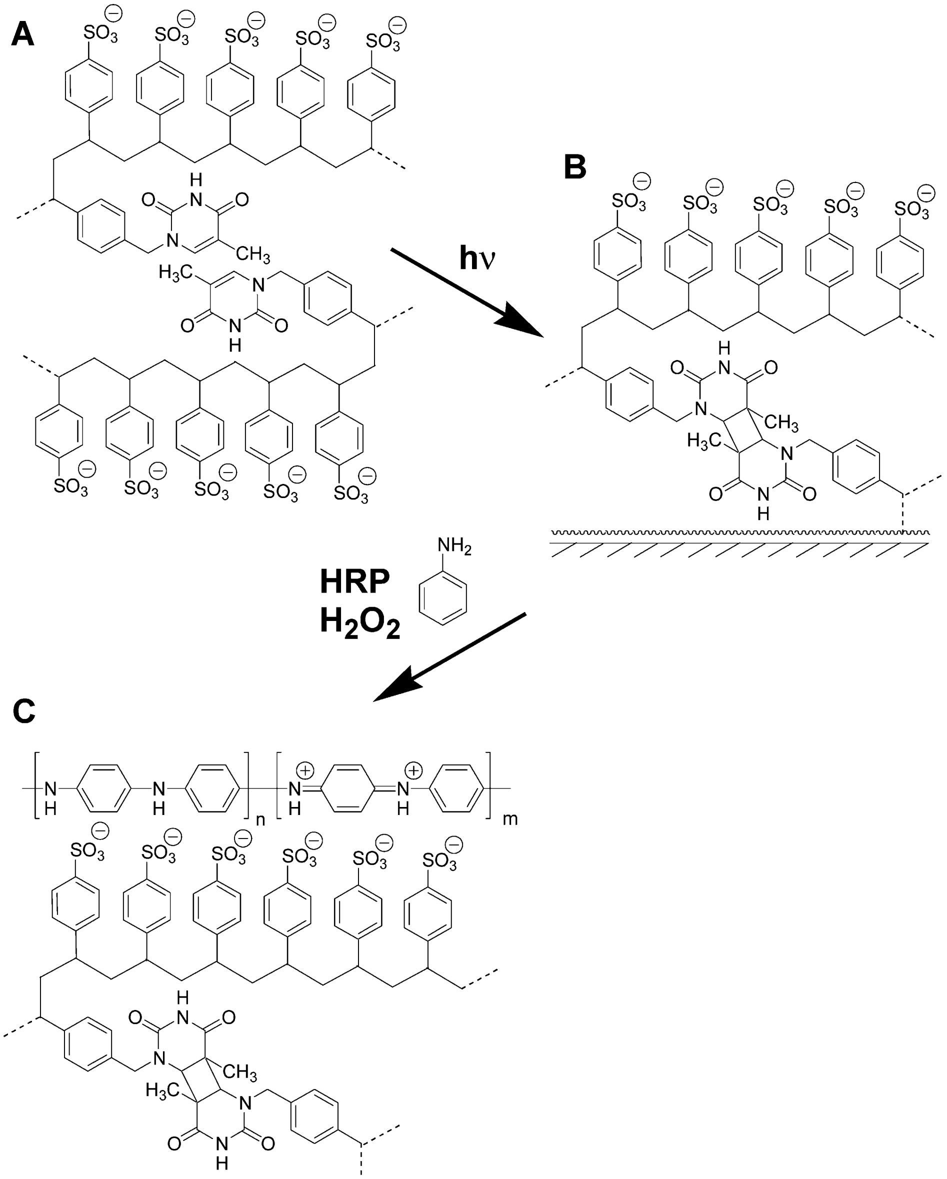
Scheme 2. Patterning Substrate with Conductive Pani[a]



[a] (A) VBT−VPS polymer before cross-linking; (B) cross-linked VBT−VPS polymer became water insoluble and as a result was immobilized on the substrate; (C) aniline polymerized on immobilized VBT−VPS yielding conductive emeraldine salt form.

413 and 850 nm, which are attributed to the polaron band transition. Its presence indicates that the polyaniline is in its doped conductive form. When the pH is increased, the solution color becomes blue, the intensity of the polaron band decreases, and a strong absorption band appears at about 580 nm, which is due to the exciton transition of the quinoid rings. Simultaneously, the intensity of the band at about 330 nm increases with increasing pH. This band is attributed to $\pi-\pi^*$ transition of the benzenoid rings in Pani. The dedoped Pani (unprotonated form) can be redoped again by adding HCl (Figure 1b). These observations are consistent with the results of the previous study where SPS was used as a template for the synthesis of electrically conducting Pani.[16] One can conclude that this patterned VBT−VPS functions as a template for conductive Pani copolymerization. Further, the presence of the VBT monomer within the VPS polymer does not interfere with the majority of the comonomer's activity.

FTIR spectra of Pani/VBT−VPS and VBT−VPS films cast from solution onto a silicon wafer are presented in Figure 2. In a Pani-containing film the bands at 1595 and 1495 cm^{-1} are due to quinone and benzene ring deformation[27] and the band at 1312 cm^{-1} is due to C−N stretching of a secondary aromatic amine.[28] Both spectra feature the band at 835 cm^{-1}, which is due to C−H out-of-plane deformations of two adjacent free hydrogen atoms in the para-substituted patterns in both VBT−VPS and Pani. The latter indicates that a head-to-tail coupling of aniline molecules occurs during polymerization.

Cyclic voltammograms of Pani/VBT−VPS complex are presented in Figure 3. Similar to the previously described Pani/SPS complex,[16] the Pani/VBT−VPS complex has two sets of

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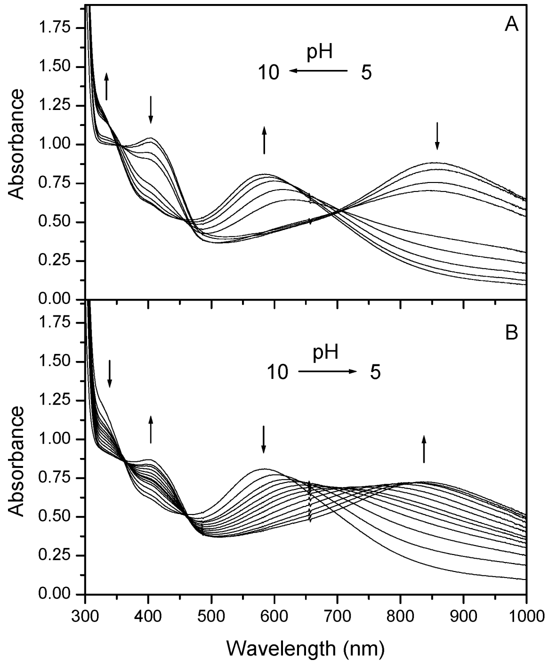

Figure 1. UV−vis spectra of Pani/VBT−VPS complex aqueous solution during titration by (A) 1 M NaOH and (B) 1 M HCl.

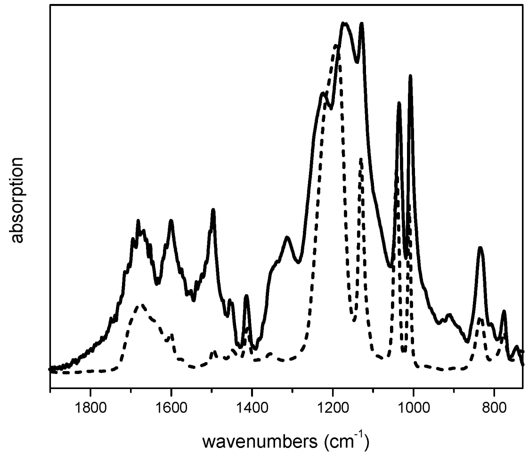

Figure 2. FTIR spectra of Pani/VBT−VPS (—) and VBT−VPS (- - -).

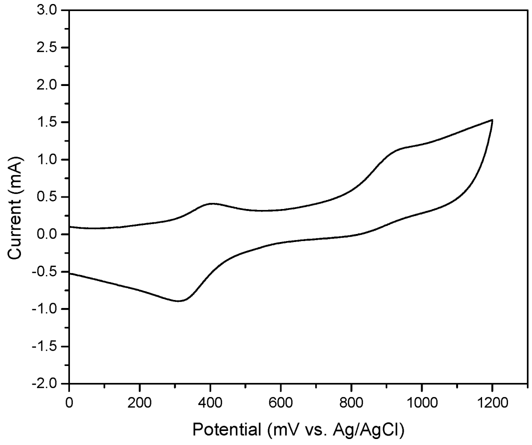

Figure 3. Cyclic voltammogram of Pani/VBT−VPS complex.

redox peaks at about 0.4 and 0.8 V. Typically three sets of redox peaks are observed with the $E_{1/2}$ at 0.17, 0.51, and 0.67 V, for Pani synthesized electrochemically in the absence of a template.[29,30] However in the presence of a template, it has been reported earlier that only one set of redox peaks at $E_{1/2}$ 0.43 V is observed.[16] The absence of one or more of the redox peaks is believed to be due to the exceptional resistance of the Pani to undergo reversible oxidation/reduction. However the cyclic voltammogram obtained for the Pani/VBT−VPS complex provides clear evidence for the presence of the electroactive Pani. Again, any concern over the deleterious influence of the VBT monomer with respect to the formation of a conductive Pani polymer is addressed by this behavior. Further, the presence of the thymine within the template does not hinder the reactivity in this system.

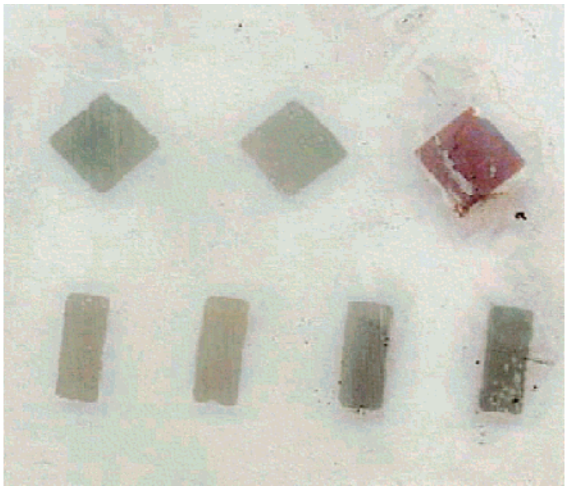

Figure 4. Pani/VBT−VPS pattern on PET substrate obtained by aniline polymerization on VBT−VPS-patterned PET. Upper right diamond was treated with NaOH.

Although the bulk conductivity of the Pani/VBT−VPS complex (measured by the four-probe method[31]) was below 10^{-6} S/cm, on doping with HCl vapor, its conductivity values increased to 5×10^{-5} S/cm. This value is comparable to the Pani/SPS complex conductivity, which is about 2×10^{-4} S/cm in the doped state. The conductivity of Pani/VBT−VPS is about 4 times lower than that of Pani/SPS, which could be attributed to the decrease in chain length of Pani, resulting from the decrease of the chain length of uninterrupted VPS sequences in the VBT−VPS relative to the SPS (or lower amount of sulfonate groups available for charge compensation during the doping process, leading to a decrease of the amount of doping) due to VBT comonomer presence in the first one. One of the possible ways to improve Pani/VBT−VPS conductivity would be to decrease the VBT to VPS ratio. Another possibility is to decrease the pH of solution used for dialysis in order to retain the Pani in the emeraldine salt form.

Surface-Selective Incorporation of Pani onto Patterned VBT−VPS. The preferred interaction between the sulfonate groups (in the patterned VBT−VPS) and protonated aniline monomer facilitated the adsorption of the latter on the pattern. Subsequently, polymerization of the monomers was accomplished using HRP and hydrogen peroxide. The pattern obtained by polymerization of Pani on the PET substrate prepatterned with VBT−VPS is shown in Figure 4. The Pani/VBT−VPS

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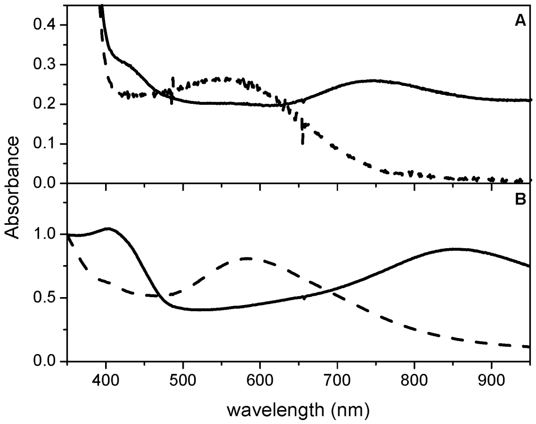

Figure 5. (A) UV−vis spectra of Pani/VBT−VPS pattern on PET substrate before (—) and after (- - -) exposure to NaOH. (B) UV−vis spectra of Pani/VBT−VPS complex aqueous solution at pH 5 (—) and at pH 10 (- - -).

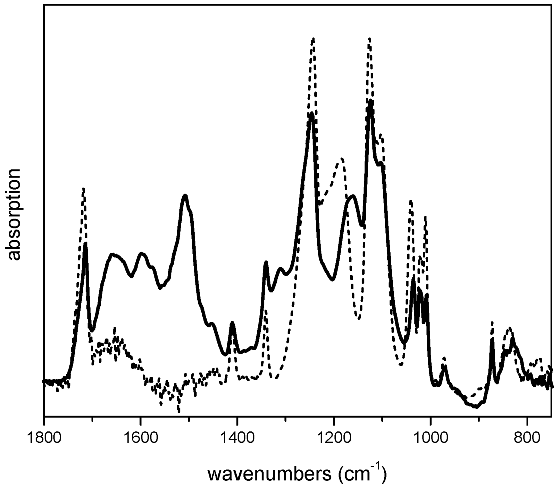

Figure 6. FTIR ATR spectra of Pani/VBT−VPS (—) and VBT−VPS (- - -) patterns on PET.

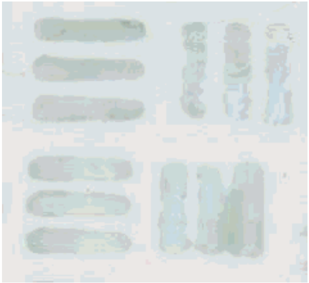

Figure 7. Pani/VBT−VPS pattern on PET substrate obtained by exposing VBT−VPS-patterned PET to Pani/VBT−VPS aqueous solution.

patterns are green, which is characteristic for the conductive emeraldine salt form of Pani except for the upper right diamond, which was treated with 1 M NaOH and became violet as a result of undoping, which is consistent with Pani transition to the emeraldine base form. It is clearly seen that aniline polymerizes selectively on the sulfonate-rich patterns forming Pani in its doped form and can be undoped while on the surface.

The thickness of the Pani/VBT−VPS layer is about 300 nm, while the thickness of the VBT−VPS layer measured prior to Pani deposition is about 100 nm. The possible explanation of this observation is that the dry, tightly coiled VBT−VPS polymer chains are partially uncoiling (swelling) when exposed to the aqueous solution, allowing aniline monomers to penetrate and align themselves along the VPS sequences while undergoing polymerization. After rinsing and drying the film the polyaniline chains remained trapped inside the VBT−VPS, preventing it from coiling back to its original size.

Figure 5A shows the UV−vis spectra of the Pani film, which was deposited from aniline solution on the VBT−VPS surface. The polaron band transition at 425 and 750 nm can be observed here as well. When the film was treated with NaOH, the Pani becomes dedoped in the same way as in the solution, and the band corresponding to the exciton transition of the quinoid rings appears at 560 nm. In Figure 5B the spectra of Pani solution at pH 5 and pH 10 are presented for comparison. A shift in the position of the absorption peak for Pani polymerized in solution as opposed to that polymerized on the substrate can be attributed to the difference in conjugation length in the Pani polymers prepared by the different methods.

Here one can conclude that VBT−VPS immobilized on the surface is a suitable template for conductive Pani synthesis. To confirm this, the ATR spectra of the Pani/VBT−VPS film on PET substrate and also of VBT−VPS on PET substrate are shown in Figure 6.

The comparison of these spectra with those in Figure 2 clearly reveals that the spectrum of Pani, polymerized on the surface, has the same features as the spectrum of Pani polymerized in solution.

Figure 7 represents a Pani pattern obtained by exposure of the VBT−VPS patterned PET substrate to a 5% aqueous solution of Pani/VBT−VPS complex for 20 min. It is clearly seen that Pani is selectively adsorbed on the sulfonated pattern on the surface rather than on bare PET. The image in Figure 4 is more intensely colored than that in Figure 7. The possible explanation of this phenomenon is that in the case where aniline is polymerized on the surface, the monomer can penetrate the small pores present in the VBT−VPS template pattern and polymerize in these pores, creating a relatively thicker Pani layer, whereas adsorption of Pani/VBT−VPS as complexed macromolecules can occur only on the VBT−VPS surface due to steric limitations.

Conclusion

A unique environmentally benign route for surface patterning with conductive polyaniline is presented. Water-soluble, photo-cross-linkable polymer was used for surface patterning and as a template for enzymatic aniline polymerization. Each step of the process was carried out in aqueous phase under near neutral pH conditions. Further investigations are underway to explore the utility of this system in a variety of applications.

Acknowledgment. The authors thank the Pfizer Corporation (Pfizer Green Chemistry Postdoctoral Fellowship) and U.S Army RDECOM Natick Soldier Center for financial support. We also thank Dr. Arthur Coury and Dr. Li Ping Yu for help with SEC/MALLS analysis, Dr. Ravi Mosurkal for performing CV measurements, Mr. Daniel W. Oblas for performing Profilometry measurements, and Mr. Kevin Dye for useful discussions.

Supporting Information Available: Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

JA042438V