Nucleophilic Substitution Reactions of Polyaniline with Substituted Benzenediazonium Ions: A Facile Method for Controlling the Surface Chemistry of Conducting Polymers

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Conducting polymers continue to be the focus of active research in diverse fields including electronics,[1] energy storage,[2] catalysis,[3] chemical sensing,[4] and biochemistry.[5] Polyaniline is one of the most well studied and industrially important conducting polymers.[6] Herein we describe a nucleophilic substitution reaction involving thin films of polyaniline (ca. 0.1 μm)[7] and 4-substituted benzenediazonium ions, resulting in poly(*N*-(4-substituted phenyl)aniline). Cyclic voltammetry demonstrates that the chemical modification destroys electroactivity of the film and proceeds via a diffusion-controlled rate-limiting step. As a result, the extent of modification can be varied by controlling the reaction time. The unmodified portion of the film remains completely electroactive with no evidence of increased resistance to charge transport into or out of the film. X-ray photoelectron spectroscopy (XPS) indicates that within the modified regions each nitrogen in the polyaniline backbone reacts in a nucleophilic substitution reaction.

Recent research in the area of conducting polymers has placed considerable emphasis on controlling both chemical and electronic properties in the bulk polymer[9−12] and at its interface.[13] It has been previously shown that the rate of nucleophilic reactions involving polyaniline can be controlled by varying the electrochemical potential of the polymer.[13] These results demonstrate that bulk chemical modification of polyaniline can be achieved in a controlled and, in some cases, reversible fashion. However, the ability to introduce a wide variety of functional groups and to control their spatial distribution within conducting polymers has yet to be demonstrated. This degree of control over the interfacial chemistry of conducting polymers will greatly impact our ability to tailor conducting polymeric materials for specific tasks ranging from sensing to electrocatalysis.

Reactions involving arenediazonium ions play an important role in synthetic organic chemistry.[14] Because of the reactivity of arenediazonium ions with nucleophiles[14] and the high concentration of diarylamines in the polyaniline backbone, it should be possible to introduce a broad range of functional groups into polyaniline using substituted arenediazonium ions. Further, because of the high concentration of diarylamines and the resistance to mass transport within polyaniline, the reaction is likely to be diffusion-controlled. A diffusion-controlled reaction should provide a means for controlling the modification of the film (i.e., the modification will occur gradually from the interface into the bulk) resulting in modified and unmodified regions, where the dimensions of these regions can be controlled by the exposure time and the diffusion coefficient of the arenediazonium ions within the film.

Chemical modification of polyaniline was achieved by immersing freshly prepared thin films[15] into a 1.0 M H_2SO_4 solution containing 50 mM of the 4-substituted benzenediazonium tetrafluoroborate salt for 5 min to 4 h without stirring (**caution**: although the tetrafluoroborate salts of substituted benzenediazonium salts are stable, other salts can be explosive). Reduction of polyaniline films[15] is required for modification since no evidence of modification was observed when the films were exposed to solutions of substituted benzenediazonium salts in their oxidized state (i.e., +0.60 V vs Ag/AgCl). The thicknesses of the thin films were varied by controlling the charge passed during the electrochemical deposition of polyaniline and were estimated in the range 0.07−0.10 μm.[7,15] The modified films were then rinsed with copious amounts of 1.0 M H_2SO_4 and characterized by XPS[16] and cyclic voltammetry.

Progress of the reaction between polyaniline and substituted benzenediazonium ions was followed by monitoring the anodic peak current from cyclic volta-

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(1) For examples of the use of conducting polymers in electronic devices, see: Burroughes, J. H.; Jones, C. A.; Friend, R. H. *Nature* **1988**, *335*, 137−141. Sailor, M. J.; Ginsburg, E. J.; Gorman, C. B.; Kumar, A.; Grubbs, R. H.; Lewis, N. S. *Science* **1990**, *249*, 1146−1149. Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477−479. Zhang, C.; Hoger, S.; Pakbaz, K.; Wudl, F.; Hegger, A. J. *J. Electron. Mater.* **1994**, *23*, 453−458.

(2) For examples of the use of conducting polymers in energy storage devices, see: Gratzel, M. *Energy Resources through Photochemistry and Catalysis*; Academic Press: New York, 1983. Conway, B. E. *J. Electrochem. Soc.* **1991**, *138*, 1539−1548. Geniès, E. M. *New J. Chem.* **1991**, *15*, 373−377. Li, F. B.; Albery, W. J. *J. Electroanal. Chem.* **1991**, *302*, 279−284.

(3) For examples of the use of conducting polymers in catalytic reactions, see: Andrieux, C. P.; Dumasbouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1982**, *131*, 1−35. Bull, R. A.; Fan, F. R.; Bard, A. J. *J. Electrochem. Soc.* **1983**, *130*, 1636−1638. Hable, C. T.; Wrighton, M. S. *Langmuir* **1993**, *9*, 3284−3290.

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(7) Film thicknesses were approximated based on the report that 33 mC cm^{-2} produces a 0.1 μm thick film of polyaniline.[8]

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(14) Zollinger, H. *Diazo Chemistry I: Aromatic and Heteroaromatic Compounds*; VCH Publishers: New York, 1994.

(15) Polyaniline films were deposited electrochemically on platinum foil (1.5 cm^2) at a constant anodic current density of 0.1 mA cm^{-2} from a solution containing 0.25 M aniline and 1.0 M sulfuric acid. Films were reduced at −0.20 V versus Ag/AgCl for 5 min prior to exposure to solutions containing diazonium ions.

(16) XPS data were obtained with a SCIENTA ESCA-300 spectrometer with a Mg Kα X-ray source ($h\nu$ = 1253.6 eV). Sensitivity factors used for C_{1s} and N_{1s} were 1 and 1.8, respectively.

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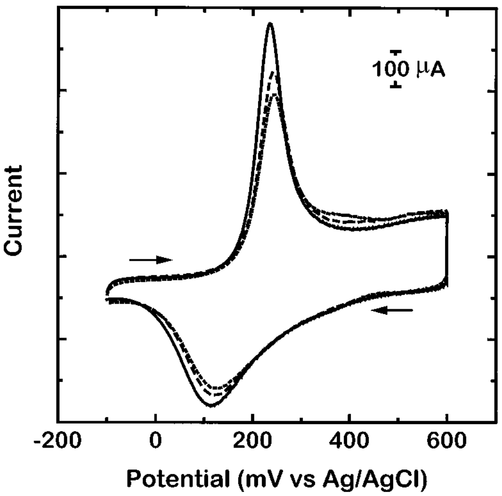

Figure 1. Cyclic voltammograms of a polyaniline thin film (grown by passing 30 mC cm^{-2} and corresponding to a film thickness of approximately 0.1 μm)[12] modified by exposure to 50 mM 4-nitrobenzenediazonium tetrafluoroborate in 1.0 M sulfuric acid for (—) 0 min, (- - -) 5 min, and (···) 15 min; scan rate = 10 mV s^{-1}.

mmetry, $i_{p,a}$, for the oxidation of the polyaniline film as a function of time (Figure 1). Since the completely modified polyaniline films were found to be electroinactive within the potential window shown in Figure 1, and since the $i_{p,a}$ of polyaniline did not decrease as a function of time in the absence of the substituted benzenediazonium ion, the anodic peak current was assumed to be proportional to the amount of unmodified polyaniline. The cyclic voltammograms in Figure 1 indicate that modification of a thin polyaniline film with 4-nitrobenzenediazonium ion does not alter the movement of charge into or out of the polymer film. For example, modification does not result in significant increases in the peak potential separation (ΔE_p) typically associated with increasing iR drops.[17] In addition, log–log plots of anodic peak current versus scan rate for both unmodified and modified films (reacted for 10 min) have slopes of 1.[18]

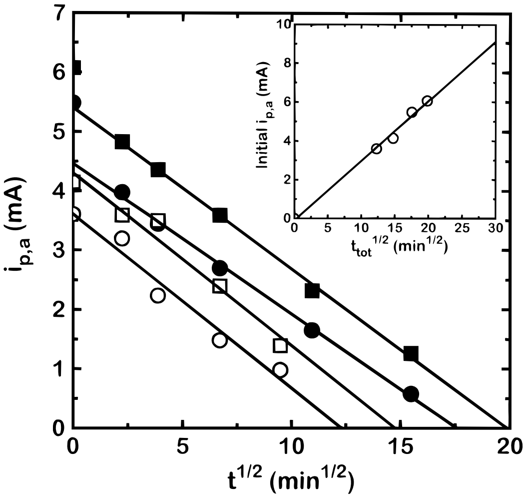

Figure 2. Plot of anodic peak current, $i_{p,a}$, versus reaction time for polyaniline thin-films (■, ●) ~0.1 μm, (□, ○) ~0.7 nm)[7] reacted with (□, ■) 50 mM 4-nitrobenzenediazonium tetrafluoroborate; and (○, ●) 50 mM 4-methoxybenzenediazonium tetrafluoroborate; in 1.0 M sulfuric acid. Inset plot of initial anodic peak current (t = 0) versus square root of the total reaction time (determined from the X intercept of $i_{p,a}$ versus $t^{1/2}$).

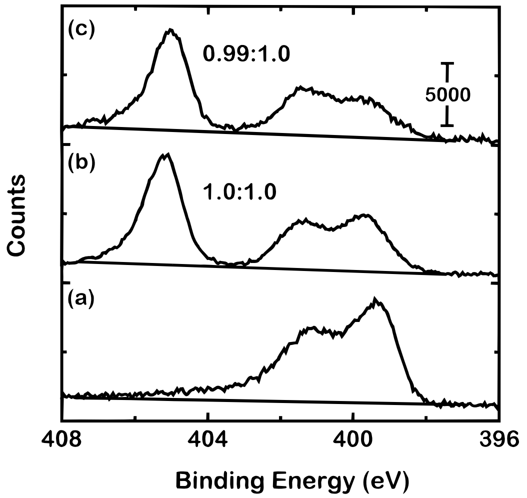

Figure 3. N_{1s} XPS core-level spectra of the polyaniline films modified in 50 mM 4-nitrobenzenediazonium tetrafluoroborate in 1.0 M sulfuric acid for (a) 0 min, (b) 10 min, and (c) 4 h. N_{1s} peak for nitro groups occurs at approximately 405 eV and N_{1s} peaks for amines in the polymer backbone occur at around 400 eV.

Linear plots of anodic peak current as a function of the square root of the reaction time (Figure 2) indicate that the modification of polyaniline with both 4-nitrobenzenediazonium and 4-methoxybenzenediazonium ions is diffusion-limited for films of different thicknesses. The similar slopes for both 4-substituted benzenediazonium ions suggest that their diffusivities are similar. An average apparent diffusion coefficient for the 4-substitued benzenediazonium ions within the polyaniline films can be estimated from the inset plot in Figure 2 by assuming that a film thickness of 0.1 μm[7] corresponds to an initial $i_{p,a}$ of 6.1 mA (grown by passing 30 mC cm^{-2})[15] and that the diffusion coefficient for the 4-substituted benzenediazonium molecule is the same in the modified and umodified polymer. Using the reaction time required to modify the film completely from Figure 2 and the equation for the root-mean-square displacement of a diffusing species,[19] $\bar{\Delta} = \sqrt{2Dt}$ (D is the diffusion coefficient (cm^2 s^{-1}) and t is the time (seconds)), an average apparent diffusion coefficient of 2.1×10^{-15} cm^2 s^{-1} is obtained. Such a small apparent diffusion coefficient indicates that these species will diffuse over very small distances as a function of time, thereby allowing a great deal of control over the modification process at the interface.

XPS spectra of the N_{1s} region obtained from polyaniline films reacted with 4-nitrobenzenediazonium ion for different times are shown in Figure 3. The N_{1s} peak area ratios of oxidized nitrogen (405 eV for the nitro group)[20] to reduced nitrogen (around 400 eV for neutral amines, protonated amines, imines, and/or azo groups that could be formed during modification)[20] were cal-

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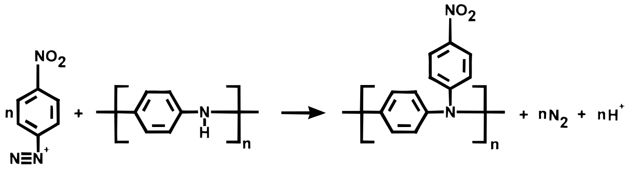
(17) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 1980; pp 569–573.

(18) log–log plots of $i_{p,a}$ versus scan rate (5–600 mV s^{-1}) gave the following linear regressions: unmodified polymer film (slope = 0.97 ± 0.03; intercept = 1.69 ± 0.05; R = 0.997; n = 10); modified film (slope = 0.96 ± 0.02; intercept = 1.58 ± 0.04; R = 0.998; n = 10).

(19) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 1980; pp 127–130.

Scheme 1



culated to be 0.0, 1.0, and 0.99 for the unmodified film and films modified for 10 min and 4 h, respectively. The C_{1s} to N_{1s} ratios in the same films were calculated to be 6.0, 5.9, and 6.1 respectively. The 1:1 ratio of oxidized to reduced nitrogen and the 6:1 ratio for carbon to nitrogen indicates that the mechanism of chemical modification is nucleophilic displacement[10] (Scheme 1). For example, if absorption of the 4-nitrobenzenediazonium ion or azo linkage formation[20] were responsible for the incorporation of nitro groups into the film, the ratio of oxidized to reduced nitrogen would be less than 1 and the ratio of carbon to nitrogen would be less than 6.

The fact that the reaction of 4-methoxybenzenediazonium ion with polyaniline is diffusion limited (Figure 2) and yet is reported to have the slowest kinetics for homogeneous nucleophilic displacement reactions in acidic solutions for a series of 4-substituted benzenediazonium ions (R = $-H$, $-CH_3$, $-C_2H_5$, $-C(CH_3)_3$, $-C_6H_5$, $-OH$, $-OCH_3$, $-Cl$, $-Br$, $-NO_2$)[21] suggests that the reactions of polyaniline with any of the 4-substituted benzenediazonium ions in the series will be diffusion-controlled. These results demonstrate that nucleophilic reactions of polyaniline with substituted benzenediazonium ions can be used to introduce a wide range of functional groups into polyaniline films. Furthermore, this approach eliminates the need for synthesizing substituted diarylamine monomers that can be used for generating N-substituted polyaniline derivatives.[22] Since the nucleophilic substitution reaction is diffusion-controlled, a great deal of control over the spatial distribution of chemical modification (on a nanometer scale) can be achieved. This control allows optimization of the chemistry of the polymer interface while maintaining the conductivity of the bulk polymer. We are currently investigating the details of the chemical, electronic, and morphological properties of the interface between the modified and unmodified polymer.

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[21] Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 783.

[22] DeArmitt, C.; Armes, S. P.; Winter, J.; Uribe, F. A.; Gottesfeld, S.; Mombourquette, C. *Polymer* **1993**, *34*, 158−162.