

## Potential-Dependent Nucleophilicity of Polyaniline

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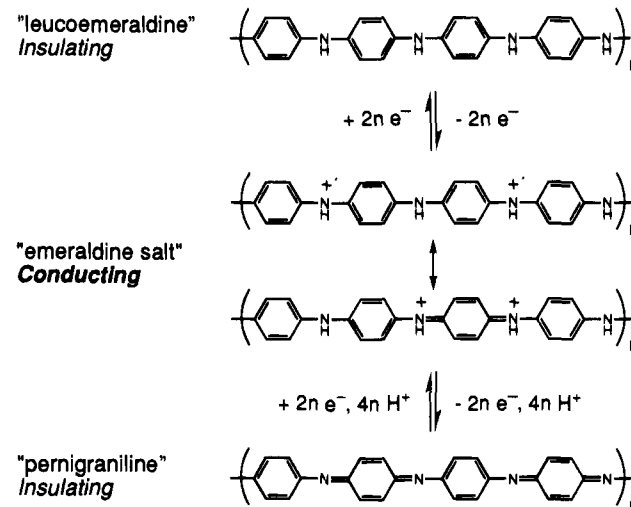
**Abstract:** The reaction of electrode-confined polyaniline with trifluoroacetic anhydride in acidified acetonitrile giving insulating and electroinactive trifluoroacetylated polyaniline has been studied by electrochemistry, reflectance IR, and microelectrochemistry. Variation of electrochemical potential from 0.2 V (reduced, most reactive) to 0.6 V (oxidized by 0.5 electron per repeat unit, unreactive) vs SCE allows control of the reaction rate. Reaction of trifluoroacetic anhydride with aniline oligomers *N*-phenylphenylenediamine and *N,N'*-diphenylphenylenediamine gave *N*-trifluoroacetylation products exclusively, exhibiting positive shifts in oligomer oxidation potential of >0.5 V, with terminal amines reacting considerably faster than internal amines. Reflectance IR following the potential-dependent growth of CO and CF<sub>3</sub> peaks for macroelectrode films of polyaniline treated with trifluoroacetic anhydride showed similar potential dependence of reactivity as conductivity measurements during trifluoroacetylation of polyaniline-derivatized microelectrode arrays. Polyaniline trifluoroacetylation was accompanied by narrowing but no shifting of the potential window of electroactivity and conductivity, and eventual elimination of all conductivity. Trifluoroacetylation of polyaniline terminal amines, rapid at all potentials, does not detectably affect conductivity. Also examined by electrochemistry were the reactions of polyaniline with other anhydrides resulting in the reactivity order (F<sub>3</sub>CCO)<sub>2</sub>O > (Cl<sub>3</sub>CCO)<sub>2</sub>O > (H<sub>2</sub>ClCCO)<sub>2</sub>O > (HCl<sub>2</sub>CCO)<sub>2</sub>O ≫ (H<sub>3</sub>CCO)<sub>2</sub>O. IR through polyaniline electrodeposited onto optically transparent Au electrodes shows that essentially complete loss of polyaniline electroactivity occurs when ≈25% of nitrogens are trifluoroacetylated. Electroactivity and conductivity of trifluoroacetylated polyaniline may be recovered by hydrolysis in K<sub>2</sub>CO<sub>3</sub>/CH<sub>3</sub>OH/H<sub>2</sub>O solution to regenerate polyaniline. Use of the reversible trifluoroacetylation of polyaniline provides a proof-of-concept for a new approach to an erasable-programmable-read-only-memory device.

## Introduction

We present results demonstrating electrochemical potential control over the reactivity of the conjugated organic conductor polyaniline. Polyaniline reacts with trifluoroacetic anhydride resulting in partial *N*-trifluoroacetylation. In this reaction, polyaniline displays a continuum of states of nucleophilicity determined by the degree of oxidation of the polymer, allowing electrochemical potential control of the rate of trifluoroacetylation, and thus control of polymer conductivity and electroactivity. In addition, the *N*-trifluoroacetyl moieties may be hydrolyzed to re-form the original conducting polymer.

Polyaniline,<sup>1–6</sup> while insulating in its colorless polybenzenoid “leucoemeraldine” reduced state, becomes conducting in acidic media when partially oxidized. The “emeraldine salt” state of polyaniline, corresponding to oxidation by 0.5 electron per repeat unit, exhibits maximum conductivity. Further oxidation to 1 electron per repeat unit gives the insulating blue-black polyquinoid “pernigraniline” state, which in all but the most anhydrous non-nucleophilic media is deprotonated.<sup>7–13</sup> Polyaniline is therefore conducting over a specific range of electrochemical potential.

## Scheme 1



This finite window of high conductivity is typical of conjugated organic conductors.<sup>9,14</sup> An interesting and unique electrical characteristic, it is the basis of a family of novel microelectrochemical devices, and we have demonstrated the preparation

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 (1) Letheby, H. J. *J. Chem. Soc.* **1862**, 161–3.  
 (2) Willstätter, R.; Dorogi, S. *Chem. Ber.* **1909**, *42*, 2147.  
 (3) Willstätter, R.; Dorogi, S. *Chem. Ber.* **1909**, *42*, 4118.  
 (4) Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1910**, 2388.  
 (5) Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1912**, 1117.  
 (6) Mohilner, D. M.; Adams, R. N.; Argersinger, W. J., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 3618.  
 (7) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.  
 (8) Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2385.  
 (9) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.

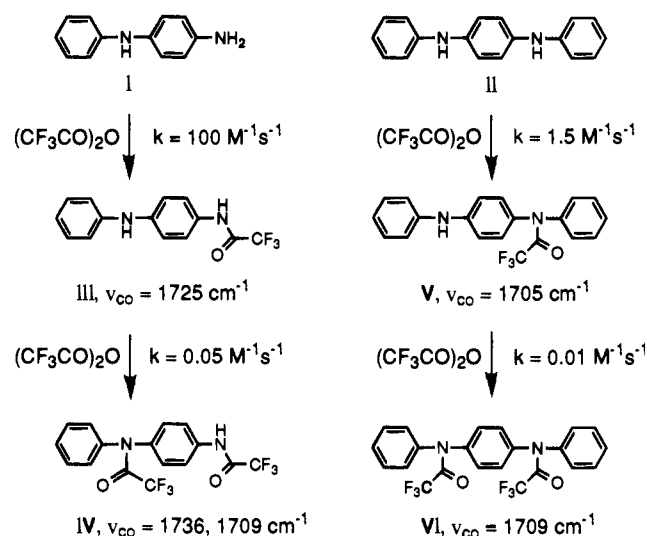
(10) Focke, W. W.; Wnek, G. E.; Wei, Y. *J. Phys. Chem.* **1987**, *91*, 5813.  
 (11) Salaneck, W. R.; Lundström, I.; Huang, W.-S.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 291.  
 (12) Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth. Met.* **1990**, *36*, 139.  
 (13) MacDiarmid, A. G.; Chiang, J.-C.; Halpern, M.; Huang, W.-S.; Mu, S.-L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173.  
 (14) Ofer, D.; Park, L. Y.; Schrock, R. R.; Wrighton, M. S. *Chem. Mater.* **1991**, *3*, 573.

of a push-pull amplifier based on two different conducting polymers with partially overlapping windows of high conductivity as the device-active materials.<sup>15</sup> It is therefore of great interest to develop methods for introducing controllable well-defined changes in conducting polymer electrochemical properties. A common route to tailoring the properties of conducting polymers is chemical modification of the monomer prior to polymerization. This approach suffers from the complication that the observed polymer properties arise from the influence of a substituent not only on polymer stereoelectronic properties but also on the polymerization reaction.<sup>16,17</sup> Poor polymerization in turn may result in lower conductivity. There are relatively few reports of altering conducting polymer properties by chemical modification *after* polymerization<sup>18-26</sup> and even fewer of which are electrochemically controlled.<sup>27</sup> The relative insolubility of most conducting polymers complicates the study of their reactivity and modification. However, when chemical modification is successful, controllable and well-defined changes in polymer behavior may be achieved which are different from those observed after electropolymerization of an analogously modified monomer.<sup>28,29</sup> In this approach, by controlling the extent of substitution on the backbone it is possible to introduce the changes in polymer properties effected by the substituent to a greater or lesser extent. It is also possible to functionalize the polymer backbone with substituents which are detrimental to, or incompatible with, polymerization. Electrochemical potential control of the oxidation state of a conducting polymer allows the electron density along the backbone to be varied continuously leading to the possibility of tuning reactivity of the polymer substrate by means of an applied voltage. We became interested in the nucleophilicity of polyaniline upon observing that its peak conductivity decayed in the presence of trifluoroacetic anhydride if the polymer was held reduced. As part of our research program to develop methods to rationally control materials properties at the molecular level and to study materials possessing electrochemically tunable reactivity, we set out to better characterize the potential-dependent reaction of polyaniline with trifluoroacetic anhydride using a combination of electrochemistry and infrared spectroscopy.

## Results and Discussion

**Reactivity of Aniline Oligomers.** In order to better interpret the spectroscopic and electrochemical data for the reaction between polyaniline and trifluoroacetic anhydride, we first examined the reactivity toward trifluoroacetic anhydride of two simple oligomeric analogs of polyaniline, *N*-phenylphenylenediamine (**I**) and *N,N'*-diphenylphenylenediamine (**II**). The results are summarized in Scheme 2.

Scheme 2



The analogs react quantitatively with trifluoroacetic anhydride at nitrogen to give amides which have characteristic absorptions in the IR at 1705 (internal amide CO), 1725 (terminal amide CO), 1230, 1200, 1160, and 1140  $\text{cm}^{-1}$  ( $\text{CF}_3$ ). At 25 °C the reaction of **I** with an excess of trifluoroacetic anhydride in a 0.2 M  $\text{CH}_3\text{CN}$  solution of trifluoroacetic acid proceeds stepwise to give *N*-phenyl-*N'*-(trifluoroacetyl)phenylenediamine (**III**) and *N,N'*-bis(trifluoroacetyl)-*N*-phenylphenylenediamine (**IV**), respectively. When 1 equiv of trifluoroacetic anhydride is added to a  $\text{CH}_3\text{CN}$  solution of 1 equiv of **I**, the only product detected by NMR, IR and GC/MS is **III**, consistent with the terminal amino group of **I** being at least 20 times more reactive than the internal amine, as is confirmed by comparison of the rate constant for initial trifluoroacetylation between **I** and **II**. The reaction of **II** with excess trifluoroacetic anhydride also proceeded stepwise to give *N,N'*-diphenyl-*N*-(trifluoroacetyl)phenylenediamine (**V**) and *N,N'*-diphenyl-*N,N'*-bis(trifluoroacetyl)phenylenediamine (**VI**). In contrast to the reactivity of pyrrole and polypyrrole toward trifluoroacetic anhydride under similar conditions,<sup>29</sup> there were no products detected resulting from electrophilic aromatic substitution at carbon.

Having established that polyaniline-like species in solution react with trifluoroacetic anhydride at nitrogen, we examined the reaction of electrode-confined polyaniline itself with trifluoroacetic anhydride. To accomplish this, polyaniline was deposited electrochemically onto flat gold macroelectrodes and onto microelectrode arrays. The resulting electrode-confined polymer allowed potential control of the oxidation state of polyaniline during reaction with trifluoroacetic anhydride and characterization of the reaction product by cyclic voltammetry, specular reflectance FTIR (RIR), and microelectrochemical conductivity measurements.

Figure 1 shows cyclic voltammetry of polyaniline electrodeposited onto two Au macroelectrodes before and after immersion under potential control into a 0.1 M  $\text{LiClO}_4/0.2$  M  $\text{CF}_3\text{CO}_2\text{H}/\text{CH}_3\text{CN}$  solution containing 1.0 M trifluoroacetic anhydride. The polyaniline held at 0.2 V vs SCE shows loss of most of its voltammetric response (without polymer loss, as demonstrated by RIR (*vide infra*)), consistent with loss of polymer conductivity. The polyaniline held at 0.5 V shows virtually no loss in response. While cyclic voltammetry of macroelectrodes provides a guide to the loss of electroactivity of the polyaniline films, characterization of the polymer by  $I_D$ - $V_G$  response is more definitive and revealing. Microelectrode arrays have proven useful in the electrochemical characterization of con-

(15) McCoy, C. H.; Wrighton, M. S. *Chem. Mater.* **1993**, *5*, 914.

(16) Diaz, A. F.; Bargon, J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Chapter 3.

(17) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(18) Rubinstein, I. *J. Electrochem. Soc.* **1983**, *130*, 1506.

(19) Manohar, S. K.; MacDiarmid, A. G.; Cromack, K. R.; Ginder, J. M.; Epstein, A. J. *Synth. Met.* **1989**, *29*, E349.

(20) Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665.

(21) Yue, J.; Gordon, G.; Epstein, A. J. *Polymer* **1992**, *33*, 4410.

(22) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.

(23) Fabre, P.-L.; Dalger, A. *J. Chem. Res.* **1991**, (S) 16, (M) 0255.

(24) Wolf, M. O.; Wrighton, M. S. *Chem. Mater.* **1994**, *6*, 1526.

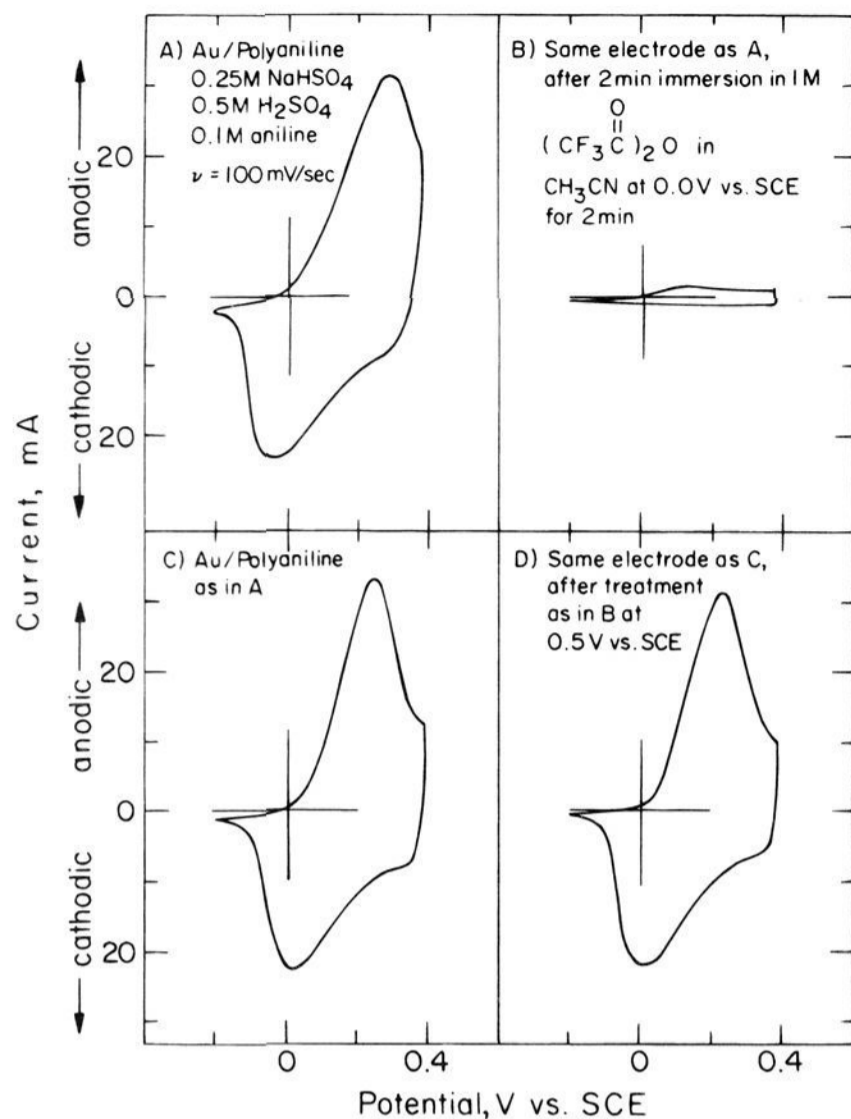
(25) Wolf, M. O.; Wrighton, M. S. Submitted for publication.

(26) Ochmanska, J.; Pickup, P. *Can. J. Chem.* **1991**, *69*, 653.

(27) Sato, M.; Fushimi, I.; Takahashi, K.; Nakaya, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2373.

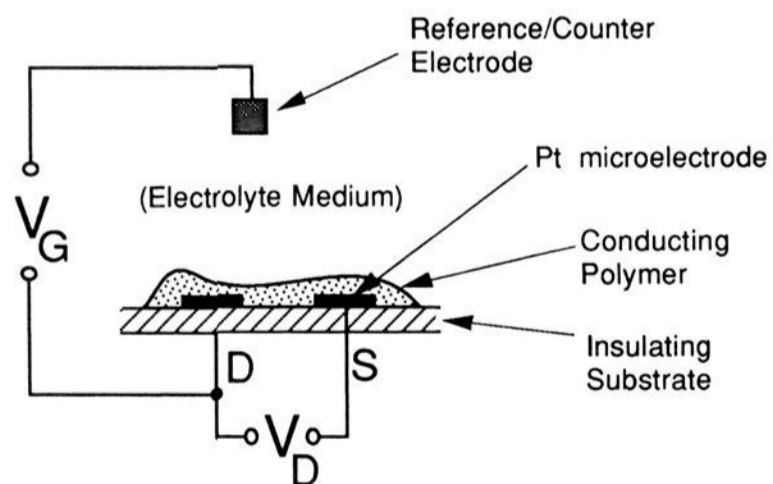
(28) McCoy, C. H.; Rozsnyai, L. F.; Wrighton, M. S. Submitted for publication.

(29) McCoy, C. H.; Wrighton, M. S. Manuscript in preparation.

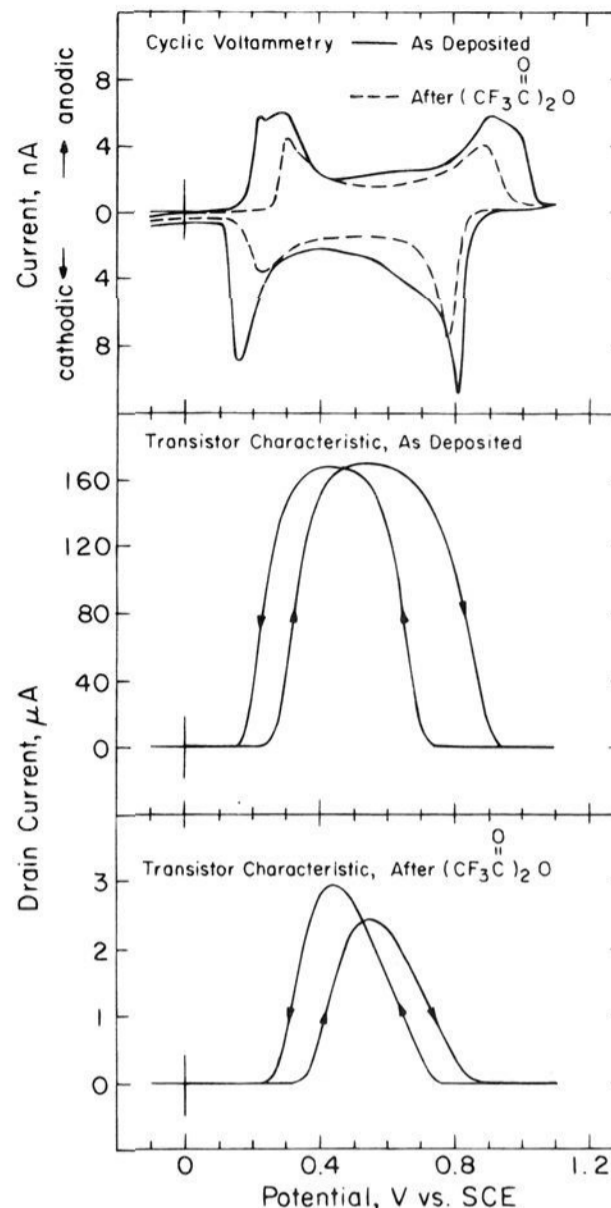


**Figure 1.** Cyclic voltammetry of polyaniline deposited onto flat gold electrodes ( $\Gamma = 1 \times 10^{-6}$  mol of aniline per  $\text{cm}^2$ ) before and after exposure to trifluoroacetic anhydride. The electrode at the top was held at 0.2 V vs SCE during exposure to trifluoroacetic anhydride while the bottom electrode was poised at 0.5 V vs SCE.

### Scheme 3



ducting polymers.<sup>7,9,14,30,31</sup> The experimental configuration, a microelectrochemical transistor, is shown in Scheme 3. The oxidation state of the polymer is controlled by gate voltage  $V_G$ , using standard electrochemical potentiostatic control. A small drain voltage,  $V_D$ , is applied between two electrodes which serve as the source and drain, and drain current,  $I_D$ , flows when the polymer is in its partially oxidized, conducting state. By scanning  $V_G$  and monitoring  $I_D$  a profile of conductivity as a function of polymer oxidation state, the  $I_D-V_G$  (transistor) characteristic, is obtained. The remarkable durability of polyaniline allows characterization of the full window of conductivity beyond the point of oxidative turn-off in a conventional electrolyte medium without serious degradation, behavior not



**Figure 2.** Cyclic voltammetry (20 mV/s) and  $I_D-V_G$  characteristics for polyaniline deposited onto three adjacent electrodes on a microelectrode array before and after treatment of the derivatized array with 1.0 M trifluoroacetic anhydride in 0.2 M  $\text{F}_3\text{CCO}_2\text{H}/0.1$  M  $\text{LiClO}_4/\text{CH}_3\text{CN}$ .

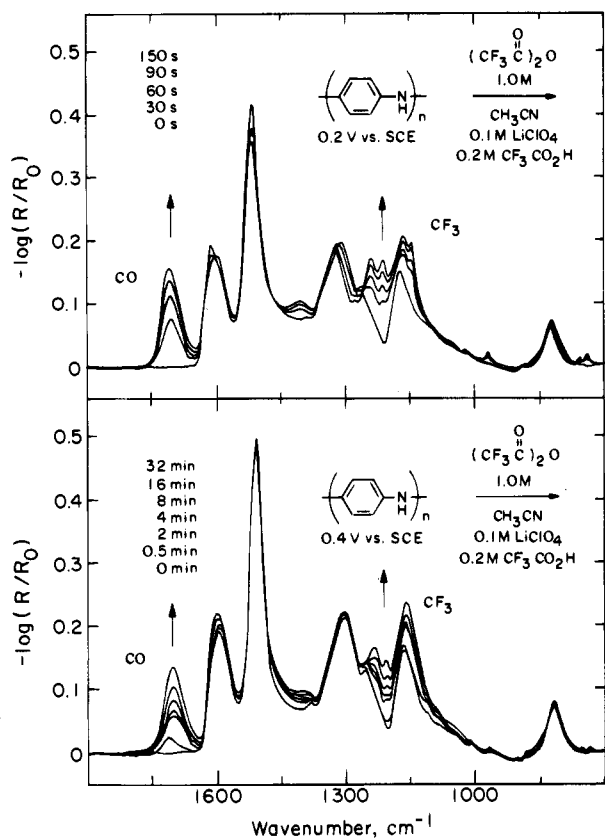
shared by other conducting polymers.<sup>9</sup> Figure 2 shows the cyclic voltammetry and  $I_D-V_G$  characteristic of a microelectrode array derivatized with electrodeposited polyaniline before and after treatment of the reduced polymer with trifluoroacetic anhydride. Changes in the cyclic voltammogram are not as dramatic as those observed in Figure 1 owing to a lesser degree of trifluoroacetylation; there is a contraction of the electroactive region of the polymer by about 100 mV and some loss in total charge passed. The  $I_D-V_G$  characteristic, however, is more dramatically affected; the peak conductivity decreases by a factor of 50, and the window of conductivity contracts symmetrically about peak conduction by about 200 mV in potential. The greater sensitivity of the  $I_D-V_G$  characteristic is not surprising as we have observed that in many other conducting polymers the  $I_D-V_G$  characteristic is affected long before any interpretable change appears in the cyclic voltammogram.<sup>32</sup> The changes in polyaniline electrochemistry upon reaction at N with trifluoroacetic anhydride are in stark contrast to those of polypyrrole upon reaction with trifluoroacetic anhydride and poly(3-methylthiophene) with  $\text{Cl}_2$ . In both of the latter cases, reaction of the electrophile with the polymer results in potential shifts of up to 0.8 V in the potential of conductivity onset but a comparatively small loss in conductivity and no loss in cyclic voltammetric response.<sup>28,29</sup>

The evolution of RIR spectra for reaction of macroelectrode-confined polyaniline at 0.2 and 0.4 V vs SCE is shown in Figure 3. Bands at  $1700\text{ cm}^{-1}$  (CO) and  $1225$ ,  $1200$ , and  $1155\text{ cm}^{-1}$  ( $\text{CF}_3$ ) grow in consistent with *N*-trifluoroacetylation of polya-

(30) White, H. S.; Kittleson, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375.

(31) Thackeray, J. W.; White, H. S.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 5133.

(32) McCoy, C. H.; Wrighton, M. S. Unpublished results.



**Figure 3.** Reflectance IR spectra for electrodeposited polyaniline on flat Au electrodes over the course of exposure to 1.0 M trifluoroacetic anhydride in 0.2 M  $F_3CCO_2H/0.1$  M  $LiClO_4/CH_3CN$ . The top electrode was poised at 0.2 V vs SCE, while the bottom electrode was poised at 0.4 V vs SCE. Spectral changes corresponding to nitrogen trifluoroacetylation can be seen in both spectra.

niline. Trifluoroacetylation for 150 s at 0.2 V vs SCE is accompanied by a decline in cyclic voltammetric response equivalent to that seen in section B of Figure 1. Note that while the reaction proceeds relatively quickly at 0.2 V vs SCE, acetylation is an order of magnitude slower at 0.4 V vs SCE where polyaniline is partially oxidized. Despite the fact that the RIR spectra in Figure 3 were taken after full electrochemical reduction of the surface-confined polyaniline, the spectra resemble those of emeraldine from other reports on the basis of the broad featureless absorbance, increasing at higher frequency (removed by baseline correction for Figure 3) and the high relative intensity of the peak at  $1600\text{ cm}^{-1}$ .<sup>33–36</sup> Spectra of fully reduced polyaniline have a flat baseline and a very weak absorbance at  $1600\text{ cm}^{-1}$ . We believe that some oxidation of the polyaniline occurs rapidly upon taking the electrode out of potential control by exposure to oxygen during rinsing and drying of the electrode.<sup>37,38</sup> There was no noticeable evolution of the RIR spectra over 30 min once the electrode was placed in the FTIR sample chamber. Figure 4 shows plots of the trifluoroacetamide carbonyl peak absorbance as a function of trifluoroacetic anhydride exposure time over a range of electrochemical potentials. There are clearly multiple states of

(33) Lu, F.-L.; Wudl, F.; Nowack, M.; Heeger, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 8311.

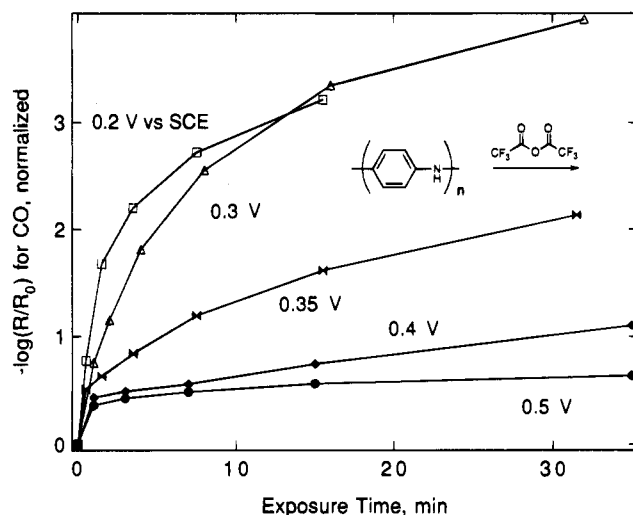
(34) Shacklette, L. W.; Wolf, J. F.; Gould, S.; Baughman, R. H. *J. Chem. Phys.* **1988**, *88*, 3955.

(35) Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988**, *24*, 231.

(36) Quillard, S.; Louarn, G.; Buisson, J. P.; Lefrant, S.; Masters, J.; MacDiarmid, A. G. *Synth. Met.* **1993**, *55–57*, 475.

(37) Mengoli, G.; Musiani, M. M.; Zotti, G.; Valcher, S. *J. Electroanal. Chem.* **1986**, *202*, 217.

(38) Wei, Y.; Hsueh, K.-F.; Jang, G.-W. *Macromolecules* **1994**, *27*, 518.



**Figure 4.** Evolution of  $-\log(R/R_0)$  for the reaction of polyaniline on Au electrodes with trifluoroacetic anhydride while poised at different potentials. The carbonyl band “absorbance” is shown as normalized to the absorbance of the unchanging polyaniline  $818\text{-cm}^{-1}$  band.

polyaniline reactivity with trifluoroacetic anhydride; the more polyaniline is oxidized the less reactive it becomes. The most obvious changes in reactivity on the laboratory time scale occur at potentials near 0.35 V vs SCE. Since the absorbance of radiation reflected from the films varied from sample to sample, we used the absorbance of the peak at  $818\text{ cm}^{-1}$  (para-substituted arene CH “flapping” mode) as an internal standard for the degree of polyaniline trifluoroacetylation, since, as Figure 3 demonstrates, absorbance of this peak changes very little over the course of trifluoroacetylation. Hence the carbonyl absorbance is shown as normalized absorbance, or the ratio of the carbonyl absorbance to that of the peak at  $818\text{ cm}^{-1}$ .

There is some confusion as to whether polyaniline, when partially oxidized in acidic media, is best described as having access to a continuum of states of charge on a molecular level, ranging from 0 to 1 electron per aniline repeat unit, or whether there are only three states—leucoemeraldine, emeraldine salt (0.5 electron per repeat unit), or pernigraniline (1 electron per repeat unit)—and “phase separated” mixtures thereof.<sup>8,34,39–46</sup> The nucleophilicity of polyaniline, as gauged by reaction rates, may shed some light on this issue. Figure 5 shows the relative rate of CO absorbance rise in Figure 4 plotted as a function of the polyaniline state of charge; the dashed curve showing hypothetical initial reaction rate linearly dependent on degree of oxidation is included for comparison. A complication encountered in generating Figure 5 is that polyaniline at a given potential becomes more reduced with a higher degree of trifluoroacetylation, especially at potentials in the vicinity of the peak current of the first redox process, as seen in Figure 2, due to anodic shift in the oxidation potential of the polymer over the course of the reaction. We estimated the fractional oxidation state of

(39) Wudl, F.; Angus, R. O., Jr.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowack, M.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3677.

(40) Baughman, R. H.; Wolf, J. F.; Eckhardt, H.; Shacklette, L. W. *Synth. Met.* **1988**, *25*, 121.

(41) Javadi, H. H. S.; Treat, S. P.; Ginder, J. M.; Wolf, J. F.; Epstein, A. J. *J. Phys. Chem. Solids* **1990**, *51*, 107.

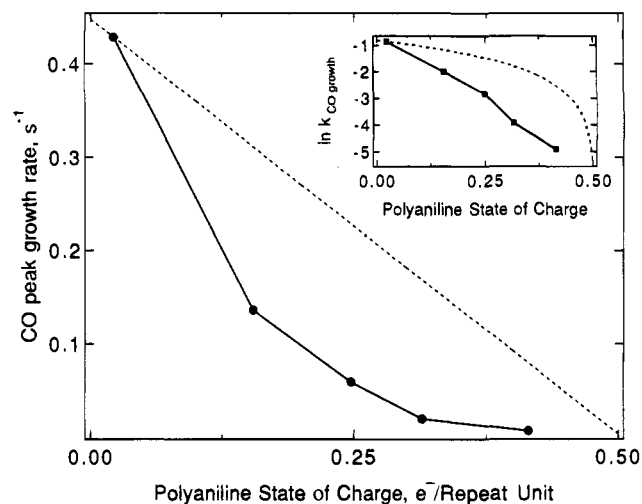
(42) Travers, J. P.; Genoud, F.; Menardo, C.; Nechtschein, M. *Synth. Met.* **1990**, *35*, 159.

(43) Shacklette, L. W.; Baughman, R. H. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 193.

(44) Glarum, S. H.; Marshall, J. H. *J. Phys. Chem.* **1986**, *90*, 6076.

(45) Genies, E. M.; Lapkowski, M. *Synth. Met.* **1987**, *21*, 117.

(46) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285.

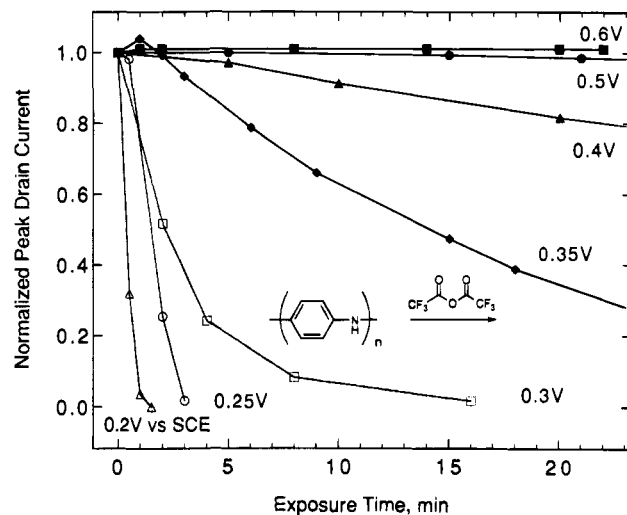


**Figure 5.** Plot of the rate of CO absorbance growth from Figure 4 versus the polyaniline state of charge, in electrons per repeat unit. The polyaniline state of charge was obtained by averaging the anodic and cathodic current of the dashed cyclic voltammogram in Figure 3 integrated to the potentials at which the samples were held. It was assumed that the degree of oxidation after the second anodic wave is 1 electron per repeat unit. The dashed line is a hypothetical reaction rate which is linearly dependent on the polyaniline oxidation state.

polyaniline using the dashed cyclic voltammogram, representing trifluoroacetylated polymer, of Figure 2, since we felt it would best represent an average of degrees of trifluoroacetylation which are followed in Figure 4.

We clearly find that the polyaniline reaction rate with trifluoroacetic anhydride deviates from a first-order dependence on the polyaniline state of charge. If the discrete states picture of the electronic structure of polyaniline at fractional oxidation states were appropriate, the rate of reaction between trifluoroacetic anhydride and polyaniline would be linearly dependent on the mole fraction of leucoemeraldine, assuming no mass-transport limitations. That is, polyaniline oxidized to 0.25 electron per repeat unit, "protoemeraldine",<sup>4</sup> should initially react half as rapidly with trifluoroacetic anhydride as fully reduced leucoemeraldine. If, on the other hand, the degree of polymer oxidation is distributed evenly over the nitrogens of each monomer unit, the state-of-charge dependence of reaction rate should be more logarithmic, and therefore more sensitive to the fractional oxidation state. Our results are therefore more consistent with the view that partially oxidized polyaniline in acidified  $\text{CH}_3\text{CN}$  has access to a continuum of charge states, rather than mixtures of the three shown in Scheme 1.

In a set of experiments carried out under identical conditions to those used for the RIR study, the change in conductivity of polyaniline upon exposure to trifluoroacetic anhydride as a function of time was determined for a series of electrochemical potentials of the polymer. The results are shown in Figure 6. Notice that loss of conductivity observed here corresponds well to the trend in the degree of trifluoroacetylation as determined by RIR. The conductivity loss occurs at a faster rate than the rise in the CO absorbance in Figure 4, indicating that even after the film is rendered insulating, further reaction with trifluoroacetic anhydride occurs. Again the transition from quick to sluggish reactivity occurs over the 0.3–0.4 V range. At 0.6 V >99.9% of the original conductivity was observed after 40 min of exposure. While potentials higher than 0.6 V were not included in Figure 6, the  $I_D$ – $V_G$  characteristic of polyaniline was stable when scanned continuously from 0.6 to 1.2 V vs SCE in the presence of trifluoroacetic anhydride. If the lower limit of the scan was moved negative of 0.6 V, a drop in



**Figure 6.** Progression of the normalized peak drain current observed in the  $I_D$ – $V_G$  characteristics of a series of polyaniline-derivatized microelectrode arrays held at the potentials indicated over the course of exposure to 1.0 M trifluoroacetic anhydride in 0.2 M  $\text{F}_3\text{CCO}_2\text{H}/0.1$  M  $\text{LiClO}_4/\text{CH}_3\text{CN}$ .

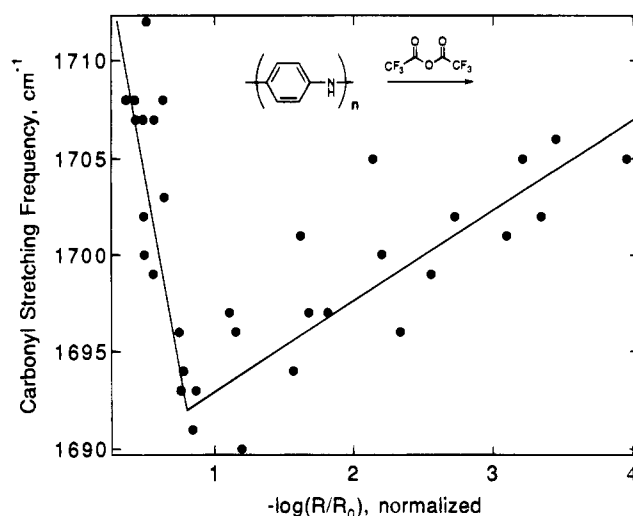
conductivity was observed on each scan of the  $I_D$ – $V_G$  characteristic. The more negative of 0.6 V the lower limit, the greater the magnitude of the loss in conductivity on each scan, as expected from the data in Figure 6. While it is possible to continuously monitor conductivity of the polyaniline during reaction with trifluoroacetic anhydride by simply applying a drain voltage across the two microelectrodes and monitoring drain current, such a measurement is complicated by the positive shift in the potential of onset of drain current upon trifluoroacetylation seen in Figure 2. This shift in the  $I_D$ – $V_G$  characteristic means that the drain current observed at a given gate voltage will shift as the potential for onset of conductivity and the  $I_D$ – $V_G$  characteristic of the polymer shift. The observed change in drain current will thus be the combination of this effect, quite pronounced in the 0.2–0.35 V range of  $V_G$ , and the loss of conductivity due to trifluoroacetylation of nitrogen. This complication is avoided by instead removing the polyaniline transistor from the anhydride cell, rinsing with water, and scanning the  $I_D$ – $V_G$  characteristic in the absence of trifluoroacetic anhydride to determine peak conductivity of the polymer at periodic intervals, a procedure which also parallels the treatment of electrodes in the RIR experiments.

Figure 2 shows that polyaniline exhibits peak conductivity at 0.6 V in acidified  $\text{CH}_3\text{CN}$ , where it is oxidized to the extent of 0.5 electron per repeat unit. The detectable changes in polyaniline reactivity with trifluoroacetic anhydride occur at more negative potentials, or lower oxidation states. Under the same conditions used for trifluoroacetylation, a more powerful or weaker electrophile than trifluoroacetic anhydride may require respectively higher or lower degrees of polyaniline oxidation to noticeably or controllably slow nucleophilic attack by polyaniline nitrogen. The reactivity of polyaniline toward acetic anhydride and its mono, di, and trichloro derivatives was characterized by microelectrode conductivity experiments in which polyaniline was exposed to a 1.0 M solution of anhydride in 0.1 M  $\text{LiClO}_4/\text{CH}_3\text{CN}$  acidified to 0.2 M of the corresponding acid (e.g. chloroacetic anhydride and chloroacetic acid). Using the rate of loss of conductivity as indicative of reaction, the following order of polyaniline reactivity with acetic anhydrides was found: trifluoro > trichloro > chloro > dichloro  $\gg$  acetic anhydride. Trifluoromethanesulfonic anhydride, a more powerful electrophile than trifluoroacetic anhydride, resulted in

complete loss of polymer from the electrode, precluding characterization. The electrochemistry and conductivity of polyaniline were stable in the presence of acetic anhydride, irrespective of the oxidation state of the polymer. As the methyl group of the anhydride becomes less electron withdrawing, reactivity is expected to decline as a result of the lower electrophilicity of the carbonyl carbon and the poorer stabilization of the acetate leaving group. This order was observed with the exception that chloroacetylation was somewhat faster than dichloroacetylation, perhaps a result of the greater bulk of the dichloromethyl group. In all cases, polyaniline was stable when held well oxidized. With the less reactive anhydrides, a lesser degree of oxidation was required to render polyaniline inert to acylation. For example, if the  $I_D-V_G$  characteristic of polyaniline is scanned in the presence of 1.0 M trifluoroacetic anhydride it is stable provided the lower limit is at least 0.6 V vs SCE. In the case of dichloroacetic anhydride, 0.3 V was sufficient and nearly complete reduction of polyaniline was required before loss of conductivity from one scan to the next became evident.

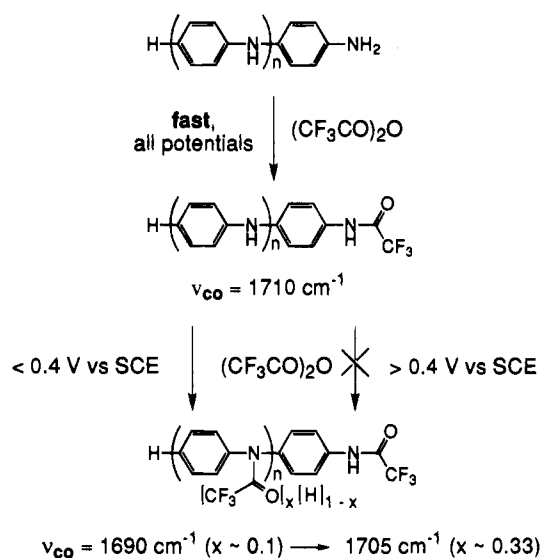
The cyclic voltammetry and  $I_D-V_G$  for polyaniline shown in Figure 2 display pronounced hysteresis, another feature typical of conjugated organic polymers which, unlike sluggish kinetics or other sources of quasi-reversibility, is essentially independent of scan rate and arises from an evolution of electronic states upon oxidation.<sup>9,44,45,47</sup> On the return scan, it is necessary to go to a more negative potential to achieve the fully reduced state of the polymer. With thick films there is also the expected normal kinetic component to response which does vary with scan rate. For polyaniline, in acidified  $\text{CH}_3\text{CN}$ , the hysteresis approaches a lower limit of about 100 mV at scan rates down to 0.2 mV/s. For all of the potential-dependent reactivity we report here, the potential was approached from the positive side, that is, during polymer re-reduction, where more negative potentials are required for full reduction of polyaniline. We expected hysteresis to cause polyaniline held at 0.35 V, where we find the greatest observable change in reactivity for potential change, approached from the reduced (negative) side to have a more negative state of charge, and therefore higher nucleophilicity, than a polymer held at 0.35 V approached from the oxidized side. We observe, contrarily, that two polyaniline-derivatized electrodes held at 0.35 V vs SCE, one brought to that potential cathodically and one anodically, have indistinguishable reactivity with trifluoroacetic anhydride over periods of up to 10 min. The implication is that, contrary to the slow scan rate cyclic voltammetry results, on the time scale of a few minutes the oxidation state of polyaniline equilibrates to a single level from the initially different states of charge arising from the hysteresis observed in the normal regime of electrochemical scan rates. Charge integration of the cyclic voltammograms in Figure 2 before and after trifluoroacetylation reveal that maximal hysteresis of 0.15 electron per repeat unit occurs at 0.2–0.25 V for the freshly deposited polyaniline, and at 0.25–0.3 V for the partially trifluoroacetylated polymer, while hysteresis at 0.35 V is lower, 0.02 and 0.09 electron per repeat unit for the polymer before and after trifluoroacetylation, respectively. Thus, polyaniline reactivity with a less reactive anhydride such as dichloroacetic anhydride may yet display hysteresis effects since the potentials for maximum observable change in reactivity for potential shift are lower, and overlap more with the region of maximum polyaniline hysteresis, where trifluoroacetic anhydride reacts too rapidly to permit examination of hysteresis effects.

An interesting difference between the RIR and microelectrode conductivity data is the fact that IR reveals a rapid, but only



**Figure 7.** Peak carbonyl stretching frequency for polyaniline treated with trifluoroacetic anhydride as a function of the extent of trifluoroacetylation. Data were taken from results shown in Figure 4.

#### Scheme 4



partial, reaction with trifluoroacetic anhydride under all conditions, but conductivity declines only when the polymer is in the more reduced states. In RIR we observe an initial, comparatively rapid appearance of a carbonyl band at  $\sim 1710 \text{ cm}^{-1}$  in the IR spectra of polyaniline electrodes which does not appear to depend on the electrochemical potential of the polymer. The expectation from a microelectrochemical measurement of conductivity would be a rapid, initial loss of drain current, and yet this is not observed. Instead, polyaniline shows only a slight and gradual loss of conductivity at 0.5 V and no loss whatsoever at 0.6 V even after 40 min. We propose that the initial potential-independent trifluoroacetylation is occurring at terminal amino groups of polyaniline, Scheme 4, and support this proposition with the following observations.

First, reaction of **I** with 1 equiv of trifluoroacetic anhydride produces only **III**, suggesting that terminal amino groups in polyaniline are also more reactive nucleophiles than their internal counterparts. Second,  $\nu_{\text{CO}}$  for the terminally trifluoroacetylated polyaniline analog **III** is  $1725 \text{ cm}^{-1}$ , about  $20 \text{ cm}^{-1}$  higher than for **IV**. Figure 7 shows a plot of trifluoroacetamide carbonyl peak frequency versus "normalized absorbance" for every data point in Figure 4. When the degree of trifluoroacetylation is low, either for short trifluoroacetic anhydride exposure periods

**Table 1.** Electrochemistry of I–VI<sup>a</sup>

	potential, V vs SCE <sup>b</sup>	<i>n</i> <sup>c</sup>
<b>I</b>	0.64	1
	0.82	1
<b>II</b>	0.94 ( <i>E</i> <sub>pa</sub> )	2
	1.34	1
	1.52	1
	0.80 (2nd scan)	<0.5
	0.70 (2nd scan)	1
<b>III</b>	1.93 ( <i>E</i> <sub>pa</sub> )	4
	2.10 ( <i>E</i> <sub>pa</sub> )	1
<b>IV</b>	0.48	1
	0.79	1
<b>V</b>	1.90 ( <i>E</i> <sub>pa</sub> )	4
	1.00 ( <i>E</i> <sub>pa</sub> )	2
	1.45 ( <i>E</i> <sub>pa</sub> )	<1
	1.73 ( <i>E</i> <sub>pa</sub> )	4
	2.07 ( <i>E</i> <sub>pa</sub> )	2
<b>VI</b>	0.77 (2nd scan)	1
	1.95 ( <i>E</i> <sub>pa</sub> )	4

<sup>a</sup> 1 mM analyte in 0.2 M CF<sub>3</sub>CO<sub>2</sub>H/0.1 M LiClO<sub>4</sub>/CH<sub>3</sub>CN at 200 mV/s at 23 ± 2 °C. <sup>b</sup> *E*<sub>1/2</sub> except as noted. <sup>c</sup> Relative peak current.

of polyaniline held reduced or for longer periods with polyaniline held oxidized, the peak frequency is high, about 1710 cm<sup>-1</sup>. Intermediate degrees of trifluoroacetylation give a lower peak frequency, down to 1692 cm<sup>-1</sup>, while more extensive trifluoroacetylation, accompanied by complete loss of polymer electroactivity, yields gradually higher peak frequencies. Consideration of the reactivity toward trifluoroacetic anhydride of **I** and **II** and the spectral features of **III**–**VI** leads us to conclude that the initial rapid trifluoroacetylation resulting in a higher  $\nu_{\text{CO}}$  is occurring at terminal nitrogens only, and that the subsequent trifluoroacetylation of internal nitrogens in polyaniline gives initially low and gradually increasing peak frequency as trifluoroacetylation makes the polyaniline backbone when fully reduced progressively more electron withdrawing.

In partially oxidized polyaniline most of the charge associated with the polymer oxidation is supported on the nitrogen atom, as depicted in Scheme 1.<sup>48</sup> Substitution at nitrogen is therefore expected to have a powerful effect on the conducting properties of the polymer. The drastic loss of conductivity upon trifluoroacetylation of nitrogen is much greater than the effect of substitution observed in *N*-alkyl- or ring-substituted polyanilines.<sup>20,49–59</sup> Table 1 shows solution electrochemical data for oligomers **I**–**VI**. The greater the degree of trifluoroacetylation of the oligomeric analogs, the more positive and irreversible their electrochemical oxidations. The fully trifluoroacetylated oligomers have redox potentials about 1.5 V more positive of their protonated precursors. The data indicate that oxidation of trifluoroacetylated polyaniline nitrogen gives a much higher

(48) Kaplan, S.; Conwell, E. M.; Richter, A. F.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 7647.

(49) Wang, S.; Wang, F.; Ge, X. *Synth. Met.* **1986**, *16*, 99.

(50) Snauwaert, P. H.; Lazzaroni, R.; Riga, J.; Verbist, J. J. *Synth. Met.* **1987**, *21*, 181.

(51) Comisso, N.; Daolio, S.; Mengoli, G.; Salmaso, R.; Zecchin, S.; Zotti, G. *J. Electroanal. Chem.* **1988**, *255*, 97.

(52) Dao, L. H.; Leclerc, M.; Guay, J.; Chevalier, J. W. *Synth. Met.* **1989**, *29*, E377.

(53) Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* **1989**, *22*, 649.

(54) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317.

(55) Wang, Z. H.; Ehrenfreund, E.; Ray, A.; MacDiarmid, A. G.; Epstein, A. J. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 263.

(56) Wei, Y.; Hariharan, R.; Patel, S. A. *Macromolecules* **1990**, *23*, 758.

(57) D'Aprano, G.; Leclerc, M.; Zotti, G. *Macromolecules* **1992**, *25*, 2145.

(58) D'Aprano, G.; Leclerc, M.; Zotti, G. *J. Electroanal. Chem.* **1993**, *351*, 145.

(59) Storrer, G. D.; Colbran, S. B.; Hibbert, D. B. *Synth. Met.* **1994**, *62*, 179.

**Table 2.** X-ray Photoelectron Spectroscopy Data for **V**, **VI**, and Polyaniline Trifluoroacetylated at 0.2 and 0.5 V vs SCE

sample	XPS integrations <sup>a</sup>		
	C <sub>1s</sub> (expected)	N <sub>1s</sub>	F <sub>1s</sub> (expected)
<b>V</b> <sup>b</sup>	13.0 (10.0)	1	1.24 (1.5)
<b>VI</b> <sup>b</sup>	14.3 (11.0)	1	2.26 (3.0)
0.2 V	11.4, 10.3 <sup>c</sup>	1	1.44, 1.36
0.5 V	11.0, 7.8 <sup>c</sup>	1	0.56, 0.40

<sup>a</sup> Corrected for element sensitivity. <sup>b</sup> Average of two runs. <sup>c</sup> Not including CO and CF<sub>3</sub> carbons.

energy cation radical than a protonated or methylated nitrogen cation radical, and thus presents a barrier to hole transport, resulting in lower conductivity than results from *N*-alkylation or ring substitution. This line of reasoning, along with the fact that **I**, which contains a terminal amine, has a higher redox potential than **II**, may also explain the potential independence of what we propose is the initial trifluoroacetylation of polyaniline terminal amino groups and the insensitivity of conductivity to terminal amine trifluoroacetylation. A partially oxidized polyaniline chain with a terminal iminium or aminium radical cation represents a less important resonance form than a chain with an internal N radical cation. The terminal amine group is therefore less coupled to the overall degree of oxidation of the polymer chain, retaining charge density and therefore nucleophilicity even when the polymer is partially oxidized. For the same reason, then, since a terminal nitrogen is not an important part of the charge delocalization in partially oxidized polyaniline, terminal amine trifluoroacetylation is not likely to affect polymer conductivity, as is observed in Figures 4 and 6.

An interesting question of broad relevance to conduction in organic polymers is what fraction of the nitrogens are trifluoroacetylated at the point at which the polymer has lost most of its electroactivity. We first attempted to address this question by X-ray photoelectron spectroscopy, XPS. Results are shown in Table 2. We used compounds **V** and **VI** as standards since they have similar chemical structure to trifluoroacetylated polyaniline. The samples "0.2 V" and "0.5 V" are the same ones studied by RIR in Figure 4, which were then exposed to trifluoroacetic anhydride for 16 and 32 min, respectively. By comparison with the oligomeric standards, the degree of trifluoroacetylation for the samples held at 0.2 and 0.5 V vs SCE is about 60% to 20%, respectively.

One limitation of XPS analysis for studying the composition of relatively thick films is that the electron mean free path limits quantitation to only the top 10–50 Å of the surface.<sup>60</sup> A more unambiguously quantitative technique for coverage measurement is transmission IR. Use of electrodes bearing a very thin layer (50–100 Å) of gold allows transmission IR,<sup>61</sup> but the resistance of the electrode itself gives rise to a voltage drop which results in a gradient of film thickness in the electrodeposited polymer which is evident to the naked eye. Beer's law therefore does not obtain. To deposit polyaniline more uniformly, electrodes were prepared with a border of conductive silver epoxy to minimize voltage drop. Polyaniline coverage was determined by cyclic voltammetry, and the electrode-confined polymer was subsequently trifluoroacetylated as above until >85% of the voltammetric response disappeared. The coverage of trifluoroacetyl groups was determined by integrating the absorbance of the trifluoroacetyl peak and dividing by the average integrated extinction coefficient per carbonyl of **III**–**VI** (determined in CH<sub>3</sub>CN) in the same frequency region. The results for two experiments were that 20 and 33% of the nitrogens in polya-

(60) Seah, M. P.; Dench, W. A. *Surf. Interface Anal.* **1979**, *83*, 391.

(61) Kang, D.; Wrighton, M. S. *Langmuir* **1991**, *7*, 2169.

niline are trifluoroacetylated when the electrochemical response is <15% of the non-trifluoroacetylated polyaniline. Since the transmission IR is sampling the entire thickness of the film, while XPS is sampling only the top 10–50 Å, we believe the coverage calculated based on cyclic voltammetry and transmission IR to be more reliable. One possible reason for the larger percentage of trifluoroacetylation calculated by XPS is the greater concentration of terminal amino groups near the surface of the polyaniline, all of which are likely to be trifluoroacetylated. While the comparison of XPS and IR data seems to point to a depth-dependent gradient in the extent of trifluoroacetylation, preliminary RIR experiments on polyaniline-derivatized macroelectrodes having different thicknesses of electrodeposited polyaniline ranging over a factor of 4, showed essentially the same potential-dependent rate of normalized CO absorbance rise shown in Figure 4, independent of thickness. We conclude that loss of >99% of conductivity occurs when  $\approx 25\%$  of the nitrogens are trifluoroacetylated.

According to Figure 4, the “normalized” value for  $-\log(R/R_0)_{\text{CO}}$  is five times larger for polyaniline films held reduced for extended periods in the presence of trifluoroacetic anhydride than for those held oxidized. Using the trifluoroacetyl coverage calculated above, and assuming that all of the terminal amino and no internal amino groups are trifluoroacetylated, we estimate that 5–6% of the nitrogens in polyaniline as we prepare it are terminal. We propose that reaction of oxidized polyaniline of known molecular weight and polydispersity in an acidic medium with trifluoroacetic anhydride followed by IR could serve as a good assay for branching,<sup>62–65</sup> since only terminal amino groups will react under these conditions.

While trifluoroacetylation of polyaniline results in nearly complete loss of electroactivity and conductivity of the polymer, the trifluoroacetyl group can be chemically removed to regenerate polyaniline. Amines are often protected as their trifluoroacetamide derivatives.<sup>66</sup> Trifluoroacetamide hydrolysis can be accomplished with potassium carbonate in 30% aqueous methanol.<sup>67</sup> This reagent was found to cleave the carbon–nitrogen bond in trifluoroacetylated polyaniline and return the polymer to its initial state displaying a typical  $I_D-V_G$  characteristic and cyclic voltammetry for polyaniline. Figure 8 shows the RIR spectral changes accompanying the cleavage reaction on a trifluoroacetylated polyaniline-coated electrode. The RIR spectrum prior to immersion in the cleavage reagent ( $t = 0$ ) shows the CO and CF<sub>3</sub> bands as seen in Figure 3. At the times noted, the electrode was removed from the cleavage solution, rinsed, dried, and characterized by RIR. Note that over the course of exposure to the cleavage reagent the CO and CF<sub>3</sub> absorptions disappear completely, while the cyclic voltammetric response returns. When the trifluoroacetylated polyaniline hydrolysis reaction has proceeded to >80% completion,  $\nu_{\text{CO}}$  remains at a low frequency (1689 cm<sup>-1</sup>), indicating that only internal trifluoroacetamides remain after longer hydrolysis periods and that the terminal amide groups are therefore hydrolyzed at least as rapidly as internal amides.

To see if the conductivity returned to polyaniline upon trifluoroacetamide hydrolysis, a microelectrode array derivatized with polyaniline was trifluoroacetylated until an  $I_D-V_G$  showed the peak conductivity to be less than 1% of its initial value.

(62) Genies, E. M.; Tsintavis, C. *J. Electroanal. Chem.* **1985**, *195*, 109.

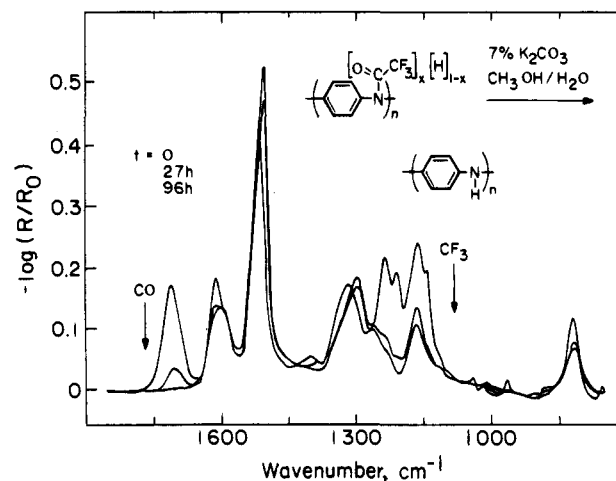
(63) Genies, E. M.; Lapkowski, M. *J. Electroanal. Chem.* **1987**, *220*, 67.

(64) Lapkowski, M. *Synth. Met.* **1990**, *35*, 169.

(65) Tshima, N.; Yan, H.; Ishiwatari, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1947.

(66) Greene, T. W.; Wuts, P. G. W. *Protecting Groups in Organic Synthesis*; Wiley: New York, 1991; pp 353–354.

(67) Newman, H. *J. Org. Chem.* **1965**, *30*, 1287.



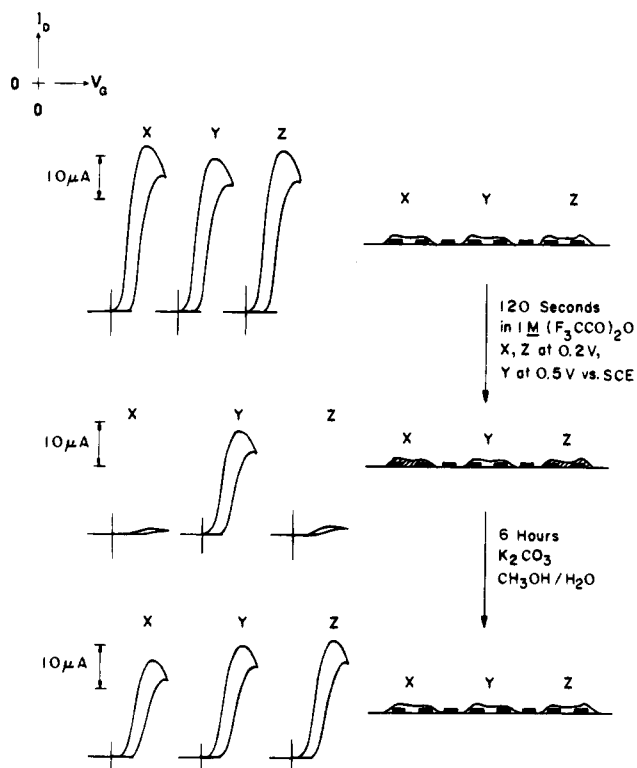
**Figure 8.** RIR spectra following the hydrolysis of trifluoroacetylated polyaniline on flat Au electrodes, showing the regeneration of polyaniline.

Immersion in the cleavage reagent for 12 h resulted in nearly complete return of conductivity. Most of the conductivity of trifluoroacetylated samples returned in the first 6 h of immersion while 18 h provided maximum recovery. Heating the cleavage solution to 50 °C gave only a minor increase in the rate of conductivity return. The recovery of conductivity in polyaniline rendered insulating by trifluoroacetylation is interesting in the context of a device known as an EPROM, or erasable-programmable-read-only-memory, the function of which is to provide a semipermanent set of information to be read and used as required but with the option of erasing (accomplished via ultraviolet irradiation of the device) and re-writing.<sup>68</sup> Shown in Figure 9 are the  $I_D-V_G$  characteristics of three polyaniline transistors, X, Y, and Z, electrodeposited side by side on an eight-electrode array of dimensions 30 × 80 μm. Transistors X and Z were held at 0.2 V in the same solution used in the trifluoroacetylation of the macroelectrodes studied above, while transistor Y was held at 0.5 V, resulting in the selective trifluoroacetylation of only devices X and Z. Immersion of the array in the same K<sub>2</sub>CO<sub>3</sub>/MeOH/H<sub>2</sub>O solution used in Figure 8 for 6 h restored conductivity to transistors X and Z. The process of trifluoroacetylation followed by hydrolysis may be repeated although the polymer does not recover complete conductivity in each cycle. Selective introduction of trifluoroacetyl groups provides a means of shutting off conductivity of any combination of specific devices allowing electrochemical “writing” of any configuration of states. Immersion in the cleavage reagent “erases” the device by restoring conductivity to the acetylated transistors. The device was “read” electrically using a circuit which provided a drain voltage and a 47 KΩ series resistor for each element. The voltage drops across the resistors (zero for insulating elements and equal to the drain voltage for conducting ones,  $V_G$  set to 0.225 V vs SCE) provided the digital (two-state) output appropriate for this sort of device.<sup>68a</sup>

In summary, we find that reaction of trifluoroacetic anhydride with the conducting polymer polyaniline confined to electrode surfaces gives trifluoroacetylation of nitrogen. The effect of polyaniline trifluoroacetylation is a drastic loss of conductivity accompanied by a narrowing of the potential window of conductivity, with no significant shift in its potential. The rate of trifluoroacetylation can be attenuated over a range of reactivities by partial oxidation of polyaniline, with a much higher than first order dependence of reactivity on the polymer

(68) Horowitz, P.; Hill, W. *The Art Of Electronics*; Cambridge University Press: New York, 1989; pp 816–817, Chapter 8.





**Figure 9.** Selective trifluoroacetylation of polyaniline transistors on a microelectrode array using electrochemical potential control. Transistors labeled X and Z are trifluoroacetylated or "written" by holding at 0.2 V vs SCE, while transistor Y is protected from reaction by being held oxidized, at 0.5 V vs SCE. The trifluoroacetylated polyanilines of transistors X and Z are then hydrolyzed by immersion in potassium carbonate in aqueous methanol, thereby "erasing" the device, restoring the conductivity of each transistor.

state of charge. Only terminal amine trifluoroacetylation, which has no effect on conductivity, is observed if polyaniline is held oxidized to 0.5 electron per repeat unit. The trifluoroacetylated polyaniline may be hydrolyzed by base to reform the original polymer with its conductivity and electroactivity restored.

### Experimental Section

All starting materials and solvents (reagent grade or better) were purchased from commercial sources and used as received except for aniline, which was distilled from  $\text{CaH}_2$ . All infrared spectroscopy was performed on a Nicolet 60SX FTIR spectrometer equipped with a liquid nitrogen cooled  $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$  detector. Solution spectra were obtained in 0.2 mm path length  $\text{CaF}_2$  or  $\text{NaCl}$  solution cells. UV-vis spectra were recorded on an HP-8452A diode array spectrophotometer. Electrochemical measurements were performed using a Pine Instruments RDE4 bipotentiostat with a saturated calomel reference electrode and platinum counter electrode, and a Kipp and Zonen BD90 XY recorder. X-ray photoelectron spectroscopy (XPS) was performed using a Surface Science Instruments (Fisons) SSL-100 spectrometer with an  $\text{Al K}\alpha_{1,2}$  source and a quartz monochromator.

**Oligomers.** Rates of reaction of **I**, **III**, and **V** with trifluoroacetic anhydride were measured at 25.0 °C in 0.2 M  $\text{CF}_3\text{CO}_2\text{H}/\text{CH}_3\text{CN}$  by monitoring UV absorbance changes with an Applied Photophysics RX-1000 stopped flow apparatus. Since under these conditions the reaction of **II** to form **V** displayed no spectral change, the rate was deduced from a competition experiment where  $(\text{CF}_3\text{CO})_2\text{O}$  (150 mg) was added under Ar to a rapidly stirred solution of **I** (190 mg) and **II** (260 mg) in 0.2 M  $\text{CF}_3\text{CO}_2\text{H}/\text{CH}_3\text{CN}$  (10 mL) at 25 °C. After evacuation of all volatiles, including  $\text{CF}_3\text{CO}_2\text{H}$ , the residue was redissolved in  $\text{CH}_3\text{CN}$ . Using an appropriate calibration solution containing **III** and **V**, the ratio of **III** to **V** formed was measured using GC/MS, integrating ions 280 and 356, respectively, and the rate constant for the trifluoroacetylation of **II** was deduced from that for **I**. Electrochemistry of **II**, **V**, and **VI**

was performed in a 0.2 M  $\text{CF}_3\text{CO}_2\text{H}/0.1$  M  $\text{LiClO}_4/\text{CH}_3\text{CN}$  solution with a 0.07  $\text{cm}^2$  glassy carbon electrode purchased from Bioanalytical Systems, Inc. XPS spectra of **V** and **VI** were obtained by casting films from  $\text{CH}_2\text{Cl}_2$  solutions onto Au-coated Si substrates.

**Infrared Spectroscopy and Reactivity under Electrochemical Potential Control.** Polycrystalline Au films for RIR were prepared by electron beam deposition of a 50 Å Ti adhesion layer followed by 1000 Å of Au on  $\text{Si}_3\text{N}_4$  coated Si wafers. Electrodes were sonicated in acetone followed by 2-propanol prior to use. Polyaniline was electrodeposited onto the bottom 2 cm of  $4 \times 1.5$  cm pieces of these wafers by cycling the potential of the immersed electrode from 0 to 0.9 V vs SCE at 100 mV/s in a freshly prepared aqueous solution of aniline (0.1 M),  $\text{NaHSO}_4$  (0.25 M), and  $\text{H}_2\text{SO}_4$  (0.5 M) until the peak anodic current at 0.2 V reached 20 mA. After cyclic voltammetric characterization of the polyaniline film by potential cycling between -0.2 and 0.4 V, an RIR spectrum of the fuzzy light green film on the electrode was obtained after emersion, copious rinsing with water, and drying under a stream of nitrogen. RIR spectra of the polyaniline films on Au were acquired with a 74° angle of incidence at 4  $\text{cm}^{-1}$  resolution. The spectra were linearly (binomial) baseline corrected, first between 2000 and 1400  $\text{cm}^{-1}$ , forcing the region between 2000 and 1750  $\text{cm}^{-1}$  to follow the baseline, and then between 2000 and 700  $\text{cm}^{-1}$ . By this method a constant is added to the absorbance at the frequencies outside the baseline correction window to retain spectral continuity. Prior to exposure to trifluoroacetic anhydride, the electrode was held briefly at the electrochemical potential to be studied in 0.1 M  $\text{LiClO}_4/\text{CH}_3\text{CN}$  acidified with  $\text{F}_3\text{CCO}_2\text{H}$  to set the oxidation state of the polymer prior to any opportunity to react with the anhydride. The electrode was then quickly immersed under potential control in a solution, temperature controlled to 25.0 °C, containing 1.0 M trifluoroacetic anhydride in a 0.2 M trifluoroacetic acid/0.1 M  $\text{LiClO}_4/\text{CH}_3\text{CN}$  solution. After the desired immersion interval, the electrode was removed from the cell and immediately washed thoroughly with water to quench residual anhydride. The cyclic voltammogram of the electrode was recorded in the aqueous deposition solution and an RIR spectrum of the rinsed, dried electrode was obtained. The electrode was then subjected to repeated cycles of exposure to trifluoroacetic anhydride and characterization allowing the progress of the reaction to be followed. The rise in CO absorbance at potentials 0.35 V and more negative was fit to a single exponential. The curves for 0.4 and 0.5 V were fit to a line. All curves were fit excluding the time zero point, since the initial absorbance rise is potential independent. Optically transparent Au films for transmission FTIR were prepared by electron beam deposition of a 50 Å Cr adhesion layer followed by 100 Å of Au onto a Si wafer. A Cu wire lead was attached to one border of  $2 \times 2$  cm squares of such a wafer using silver epoxy, which was also applied around the entire perimeter of the square. After curing, the silver epoxy border was covered with insulating white epoxy, leaving an effective electrode of dimensions  $14 \times 14$  mm. Polyaniline deposition and reaction under potential control was performed as described above for the reflectance electrodes.

Trifluoroacetamide cleavage reactions were carried out by immersion of the trifluoroacetylated polyaniline-coated electrode in 7%  $\text{K}_2\text{CO}_3/5:2$   $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  at room temperature. Over the course of the reaction the polymer gradually turned deep purple. After exposure to the cleavage reagent, the electrode was rinsed with water and characterized in 0.5 M  $\text{H}_2\text{SO}_4$  where the normal electrochromic response expected for polyaniline was observed.

**Microelectrochemistry.** Arrays of eight individually addressable, platinum band microelectrodes,  $1.5 \times 80$   $\mu\text{m}$ , separated by 1.5  $\mu\text{m}$ , were fabricated by conventional photolithographic and metalization techniques.<sup>30,31</sup> The electrodes were cleaned prior to derivatization by cycling in 0.5 M  $\text{H}_2\text{SO}_4$  from -0.3 to 1.2 V vs SCE. Polyaniline was deposited onto pairs of adjacent electrodes as described above until current for the polymer oxidation wave reached 12 nA.  $I_D-V_G$  characteristics were obtained by sweeping the potential of the two adjacent polyaniline-coated microelectrodes (connected to the K1 and K2 working electrode terminals of an RDE4 bipotentiostat) between 0 and +1.1 V vs SCE with a 25 mV drain voltage applied as a negative offset on K2. Polyaniline deposited onto microelectrodes was trifluoroacetylated and subsequently hydrolyzed under the same conditions as the macroelectrodes. The microelectrode device represented in

Figure 9 was prepared by simultaneous deposition of polyaniline onto three pairs of electrodes leaving the third and sixth electrodes unmodified to obtain three independent transistors. The read circuit for the device consisted of 47  $K\Omega$  resistors in series with each of the three transistors with a drain voltage of 100 mV applied to all three resistor-transistor pairs. Reactions with other anhydrides were carried out at room temperature in solutions of 1.0 M anhydride and 0.2 M of the corresponding acid in 0.1 M  $\text{LiClO}_4/\text{CH}_3\text{CN}$ .

**Synthesis. (a) *N*-(trifluoroacetyl)-*N'*-phenylphenylenediamine (III).** Trifluoroacetic anhydride (2.10 g, 10.0 mmol) was added dropwise to a rapidly stirred solution of *N*-phenylphenylenediamine (I: 1.84 g, 10.0 mmol), in  $\text{CH}_3\text{CN}$  (20 mL). Volatiles were removed and the residue was redissolved in  $\text{CH}_2\text{Cl}_2$  and chromatographed on a short silica column, eluting with  $\text{CH}_2\text{Cl}_2$ . Calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{OF}_3$ : C, 60.00; H, 3.96; N, 9.99. Found: C, 59.31; H, 3.81; N, 9.86. IR ( $\text{CH}_3\text{CN}$ ) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 3365 (180, NH), 3318 (140, NH), 1722 (670, CO, relative oscillator strength per CO = 1), 1599 (480), 1558 (220), 1519 (720), 1497 (450), 1319 (250), 1289 (290), 1252 (300), 1237 (230,  $\text{CF}_3$ ), 1201 (360,  $\text{CF}_3$ ), 1154  $\text{cm}^{-1}$  (860,  $\text{CF}_3$ ).  $^1\text{H-NMR}$  (acetone- $d_6$ ):  $\delta$  10.09 (b, 1H, (CO)NH), 7.59 (d,  $J$  = 8.8 Hz, 2H), 7.48 (b, 1H, PhNHPh), 7.23 (t,  $J$  = 7.4 Hz, 2H), 7.13 (m, 4H), 6.85 (t,  $J$  = 7.2 Hz, 1H). UV-vis ( $\text{CH}_3\text{CN}$ ): 302 nm (23000).

**(b) *N,N'*-Bis(trifluoroacetyl)-*N*-phenylphenylenediamine (IV).** Trifluoroacetic anhydride (6 g, 29 mmol) was added to a stirred solution of I (2 g, 11 mmol). After 5 min the volatiles were removed and the residue was taken up in  $\text{CH}_2\text{Cl}_2$  and chromatographed on a short column of silica, eluting with  $\text{CH}_2\text{Cl}_2$ . The product was isolated as an amorphous glassy solid. Calcd for  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2\text{F}_6$ : C, 51.07; H, 2.68; N, 7.44; F, 30.30. Found: C, 50.41; H, 2.74; N, 7.44; F, 28.93. IR ( $\text{CH}_3\text{CN}$ ) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 3301 (120, NH), 1736 (560, CONH), 1726 (620, CONH), 1709 (920,  $\text{CONAr}_2$ , relative oscillator strength per CO = 1.11), 1610 (160), 1594 (130), 1553 (360), 1513 (470), 1493 (270), 1286 (240), 1231 (880,  $\text{CF}_3$ ), 1205 (1130,  $\text{CF}_3$ ), 1157  $\text{cm}^{-1}$  (1500,  $\text{CF}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.76 (b, 1H, NH), 7.6–7.2 (m, 9H). UV-vis ( $\text{CH}_3\text{CN}$ ): 254 nm (17000).

**(c) *N*-(Trifluoroacetyl)-*N,N'*-diphenylphenylenediamine (V).** Trifluoroacetic anhydride (2.10 g, 10.0 mmol) was added to a rapidly stirred solution of *N,N'*-diphenylphenylenediamine (2.60 g, 10.0 mmol) in  $\text{CH}_3\text{CN}$  and the product was worked up as for III. An analytical sample was prepared by recrystallization from  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ . Calcd for  $\text{C}_{20}\text{H}_{15}\text{N}_2\text{OF}_3$ : C, 67.41; H, 4.24; N, 7.86. Found: C, 67.59; H, 4.57; N, 7.89. IR ( $\text{CH}_3\text{CN}$ ) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 3386 (180, NH), 1705 (800, CO, relative oscillator strength per CO = 1.20), 1597 (540), 1519 (620), 1498 (550), 1323 (310), 1232 (640,  $\text{CF}_3$ ), 1203 (660,  $\text{CF}_3$ ), 1159 (510,  $\text{CF}_3$ ), 1140  $\text{cm}^{-1}$  (530,  $\text{CF}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.4–7.0 (m, 14H), 5.88 (b, 1H, NH). UV-vis,  $\text{CH}_3\text{CN}$ : 294 nm (23000).

**(d) *N,N'*-Bis(trifluoroacetyl)-*N,N'*-diphenylphenylenediamine (VI).** Trifluoroacetic anhydride (6 g, 29 mmol) was added to a stirred solution of *N,N'*-diphenylphenylenediamine (2.6 g, 10 mmol) in  $\text{CH}_3\text{CN}$  and the product was worked up as for IV. An analytical sample was prepared by recrystallization from EtOH. Calcd for  $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_2\text{F}_6$ : C, 58.41; H, 3.12; N, 6.19. Found: C, 58.29; H, 3.24; N, 6.19. IR ( $\text{CH}_3\text{CN}$ ) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 1709 (1390, CO, relative oscillator strength per CO = 1.06), 1594 (200), 1507 (400), 1492 (500), 1229 (1130,  $\text{CF}_3$ ), 1205 (1230,  $\text{CF}_3$ ), 1161 (960,  $\text{CF}_3$ ), 1146  $\text{cm}^{-1}$  (720,  $\text{CF}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.45–7.3 (m). UV-vis ( $\text{CH}_3\text{CN}$ ): 276 nm (6400) (s), 236 nm (18000).

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