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Electrochemical and Ultraviolet–Visible Spectroelectrochemical Investigation of Selectivity of Potentiometric Gas Sensors Based on Polypyrrole

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It is shown that electrochemical incorporation of nitrotoluenes into the polypyrrole matrix changes profoundly the electron work function of this material as compared with plain polypyrrole. Simultaneously this material exhibits selective sensitivity to aromatic compounds. The presence of the nitroarenes in the polypyrrole matrix has been confirmed spectroelectrochemically.

It has been shown in previously (1, 2) that a suspended gate field transistor (SGFET) can be used as a general device for sensing of gases and dielectric fluids. The principle of operation of this device is based on chemical modification of the electron work function of a chemically selective layer which is electrochemically deposited within the gate structure of the device.

Electropolymerized polypyrrole (PP) can be used as a general matrix into which other chemical functionalities can be incorporated in order to change its selectivity. It has been shown that other organic compounds can be incorporated electrochemically into the bulk of the PP film (3) and that its surface can be covalently modified (4). Furthermore, PP forms an ohmic junction at noble metal electrodes (5), which is important for the proper operation of the device (1). In this paper we shall describe the correlation between the spectroelectrochemical characteristics of various types of layers based on PP and their sensitivity and selectivity to some aromatic and hydrogen bonding compounds that interact with the film by hydrogen bonding or through aromatic π systems.

While pyrrole undergoes slow oxidation at room temperature and atmospheric pressure (6), polypyrrole with BF_4^- anion is remarkably stable after the initial reaction with air. Practically no thermal degradation of the PP has been observed below 130 °C (7). This means that, if necessary, these devices could be used even at moderately elevated temperatures. In this study the operating temperature of the transistor was only 25 °C.

EXPERIMENTAL SECTION

Suspended gate transistors with an approximately 2000 Å gap were fabricated and encapsulated as described previously (1). Encapsulated devices were first etched in solution containing 15 mL of H_2O_2 (30%), 50 mL of 0.1 M EDTA, and 10 mL of concentrated NH_4OH for 10 min in order to remove traces of residual titanium and tungsten from all surfaces within the gate. Before electrodeposition the Pt gate was conditioned electrochemically by cycling between −0.25 and +1.25 V at 10 V s⁻¹ in 1 M H_2SO_4 for 10 min. Cyclic voltammograms obtained after this pre-

treatment were identical with those described by Arvia et al. (8). After this step the devices were dried in an oven at 60 °C for 12 h.

The electrodeposition was carried out by applying current pulses supplied from an IBM EC 225 potentiostat operated in the normal pulse mode. The repetition rate was set at 5 s, the pulse amplitude was 100 mV, and the scan rate was 10 mV/s. The initial and final potentials were +0.6 and +0.9 V, respectively, unless specified otherwise. The deposition current was integrated with an analog integrator (constructed in these laboratories) until a total charge of 10 μC/gate had been passed. In all experiments the reference electrode was Ag/0.1 M $AgNO_3$ in acetonitrile and the basic reaction solution was 0.1 M pyrrole with 0.1 M tetrabutylammonium tetrafluoroborate (TBAF) as the supporting electrolyte.

Threshold voltage shifts and the basic transistor characteristics were measured with a Hewlett-Packard semiconductor parameter analyzer, Model 4145A. Chemical response measurements were made in constant current mode, in saturation (V_{DS} = 4.0 V and I_{DS} = 280–350 μA).

The test chamber was attached to the outlet of a Perkin-Elmer Sigma 2000 gas chromatograph and was maintained at room temperature. The carrier gas was nitrogen (typical flow rate was 25 mL min⁻¹). The output from the SGFET monitor was digitized and stored in a Perkin-Elmer 7500 professional computer equipped with a LCI-100 laboratory integrator.

For the spectroelectrochemical experiments the aforementioned polymers were electrodeposited in the same manner as described above (for Pt-wire electrodes) onto 7-mm-diameter platinum-disk mirror electrodes. These polymer modified electrodes were mounted in a spectroelectrochemical kinetic cell as described previously (9). Reflectance spectroelectrochemical spectra were obtained for the films by using the modulated specular reflectance spectroscopic (MSRS) method (9). This procedure involves measurement of the difference spectrum between two potentials (see Figure 2 legend) of absorbing species generated electrochemically at those potentials. The lower (base) potential was held at a potential where no redox processes occurred. The pulsed (higher) potential was chosen to cause either oxidation or reduction of the PP film. The potential pulse modulation at 40 Hz was supplied by a fast rise-time, three-electrode potentiostat and waveform generator (JAS Instruments). The resulting ac reflectance change was monitored with a phase-sensitive detector (Bentham). The wavelength was scanned throughout the UV–visible region by using a xenon arc source (Photon Technology International) and a monochromator (GCA McPherson 300). The resulting difference spectra (detected by a photomultiplier, RCA 31000A) were recorded on a plotter. Negative absorption bands correspond to absorbing species present at the higher potential, while positive bands are indicative of absorbers prevalent at the lower base potential.

A MSRS spectrum of the nitrobenzene radical anion was also recorded for reference. The base potential was first held at a voltage where no faradaic process occurred and then stepped to a value where nitrobenzene was reduced to its radical anion at a diffusion-limited rate. The difference spectrum was recorded as was previously described for the polymer films.

Table I. Threshold Voltage Shifts and Responses of SGFETs with Polypyrrole Film Deposited under Different Conditions

| deposition conditions	V_T shift	response
acetonitrile (Ac)	−0.284	Ac(−)
methanol	+0.776	Ac(−)
1 M toluene (T), Ac	+0.275	Ac (+)
1 M nitrobenzene, Ac	+0.712	Ac (++)
1 M 2-nitrotoluene, Ac	+6.503	Ac (++), T (++++)
1 M 3-nitrotoluene, Ac	+8.700	Ac (++), T (+)
1 M 4-nitrotoluene, Ac	+7.500	Ac (−−−−), T (−−−)

RESULTS

Electrochemistry. Suspended gate field effect transistors (SGFET) coated with polypyrroles (PP) prepared under different conditions have shown markedly different selectivities to various gases and a large variation in the threshold voltage shift ΔV_T, which is related to the change in the electron work function of the polypyrrole layer (1). The threshold voltage shifts for SGFETs with various PP layers measured with respect to bare, cleaned Pt in air at room temperature are summarized in Table I together with a qualitative description of their selectivity. In order to characterize these films, we have used both cyclic voltammetry and spectroelectrochemistry. The cyclic voltammograms for PP codeposited with 4-nitrotoluene and with nitrobenzene are shown in Figure 1. It is interesting to note that the voltammetry corresponding to the reduction/oxidation of the nitro groups ($E_{1/2}$ approximately −1.1 to −1.2 V) can be seen in nitrotoluenes (only 4-nitrotoluene is shown in Figure 1A) even after repeated cycling between the reduced and oxidized form of PP. The results are similar to the reduction of poly(N(p-nitrophenyl)pyrrole) investigated by Diaz et al. (4). The V_T shifts of PP/nitrotoluenes are strongly positive (~+8 V) indicating a substantially increased electron affinity of this material as compared with ordinary PP. On the other hand, the V_T shift for the PP/nitrobenzene is only moderately positive and the redox pattern of the nitro group in PP/nitrobenzene can be seen only if the cycling is limited to between 0 and −2.5 V (Figure 1Ba). When the PP is oxidized (Figure 1Bb), the nitro group redox wave is lost after only a few cycles and only oxidation (E_p = +0.8 V) and reduction (E_p = −0.2 V) are seen (Figure 1C).

Spectroelectrochemistry. The MSRS spectra for the five films shown in Figure 2 were discussed in the Experimental Section. These spectra were taken in 0.1 M TBAF/acetonitrile. For each film the difference spectra were recorded with reference firstly to a pulse sequence −0.60 V to −2.40 V (vs. Ag/Ag$^+$), secondly −0.60 V to +1.20 V, and thirdly −0.60 V to −2.40 V again. This sequence was chosen in an effort to determine differences in the films caused by film oxidation. First the films were reduced, and difference spectra at 40 Hz modulation were recorded (Figure 2a). The spectra for the oxidations were then recorded (Figure 2b). Finally, the spectra for the reductions were again obtained (Figure 2c), and any changes in bands due to film alteration caused by oxidation were noted.
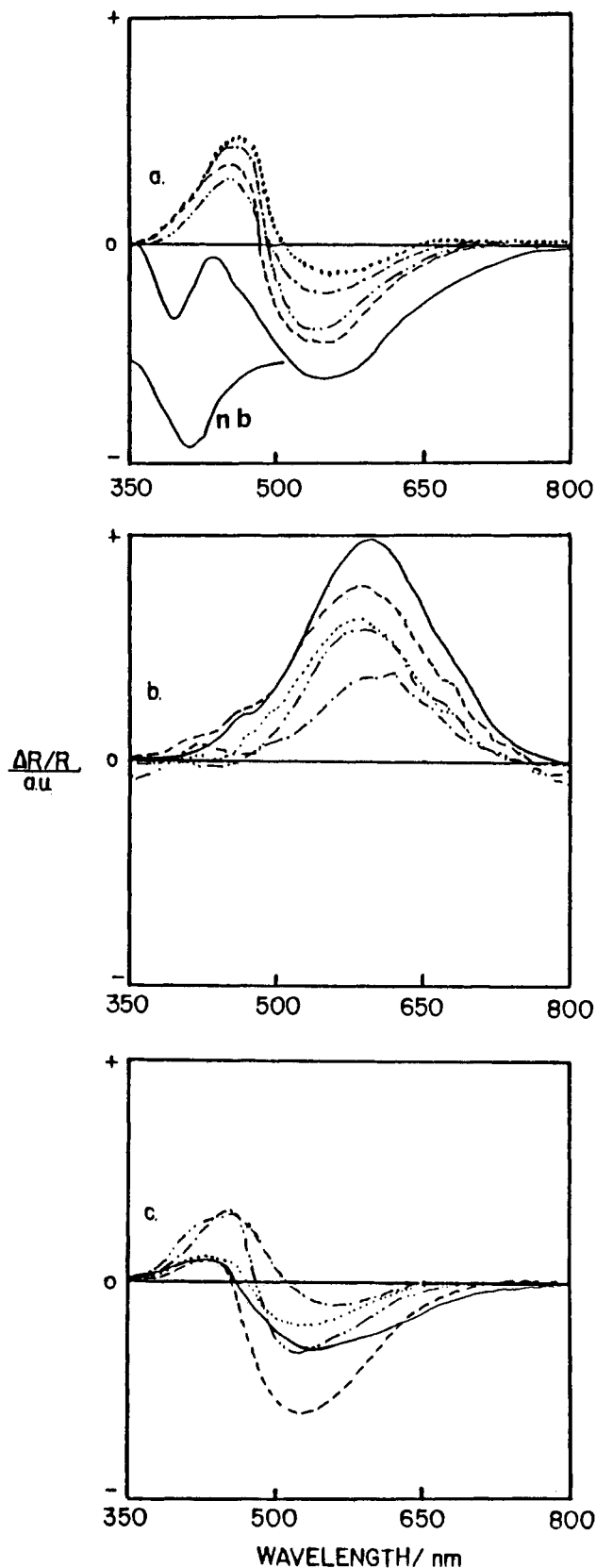
The difference spectrum resulting from the reduction of PP/nitrobenzene film (Figure 2a) differs from those obtained for the other four films; a negative peak at 395 nm appears in the nitrobenzene/polypyrrole spectrum. The difference spectra for the oxidations of the five films are all quite similar (Figure 2b). Subsequent to oxidation, spectra for reductions were again recorded (Figure 2c). The spectra for the five films then appeared similar. The negative peak at 395 nm in the nitrobenzene/polypyrrole film has disappeared as a consequence of the oxidation excursions undergone during the recording of the spectrum in Figure 2b.
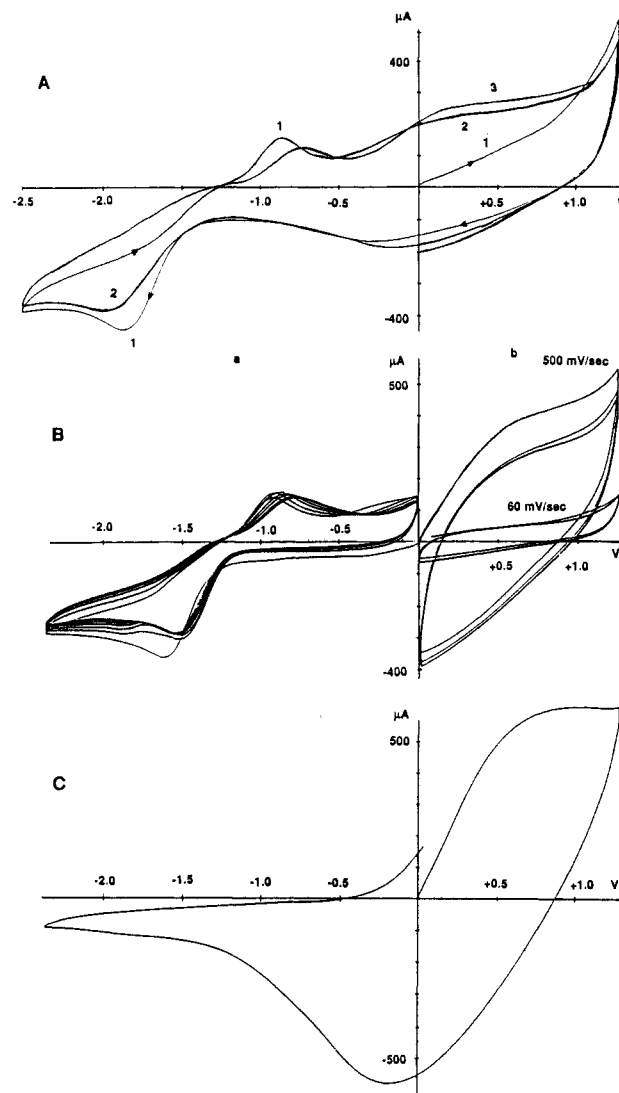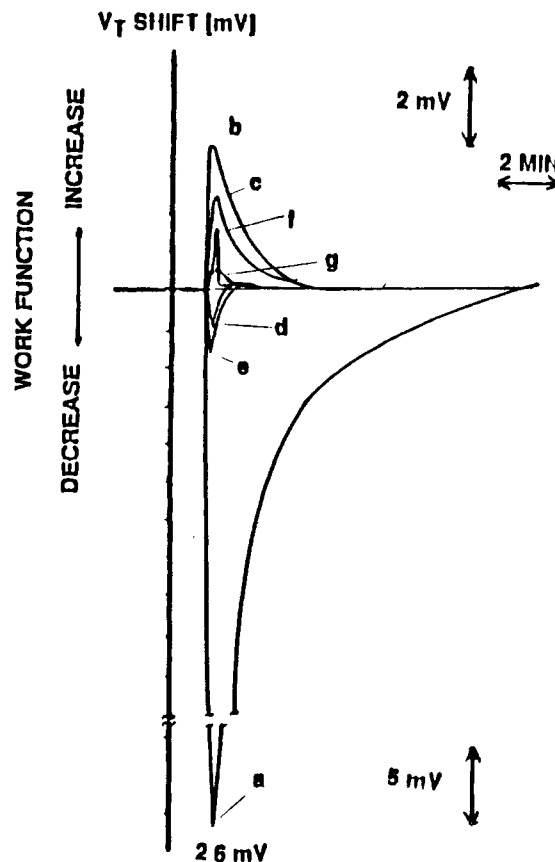

Figure 1. Electrochemical behavior of PP/nitroarene layers prepared on Pt-disk electrode (3 cm²) from a 1 M nitroarene, 0.1 M pyrrole, and 0.1 M TBAF/acetonitrile solution. After deposition the electrode was rinsed and transferred to fresh 0.1 M TBAF acetonitrile solution. The scan rate was 0.5 V s⁻¹. The scan direction is indicated by arrows. Electrochemical behavior shown for (A) PP/4-nitrotoluene; (B) PP/nitrobenzene cycled first (a) between ±0 and −2.4 V, then (b) between 0 and +1.3 V; and (C) the first cycle between +1.3 and −2.4 V for PP/nitrobenzene.

The MSRS spectrum of nitrobenzene radical anion is shown in Figure 2a (insert). A single negative Lorentzian shaped peak is seen with a maximum in acetonitrile at 447 nm, somewhat shifted from the maxima seen in dimethylformamide (DMF) (10) and sulfolane (11), where peaks due to nitrobenzene anion radical were observed at 464 and 465 nm, respectively. Neutral nitrobenzene does not absorb in this wavelength region.

Chemical Response. The overall response of the SGFET coated with PP or nitroarene modified polypyrroles parallels the electrochemical observations; all transistors with PP matrix respond to alcohols and to acetonitrile. However, the polarity of the response to acetonitrile as well as its amplitude varies for different PP (Figure 3). The response to methanol is always higher than to acetonitrile; however, the response is somewhat affected by the solvent used for the electrodeposition (Figure 4). Transistors with PP deposited from acetonitrile show preference to methanol over acetonitrile with the ratio of response 5.2, whereas for SGFET with PP deposited from methanol this ratio is 8.0, indicating increased affinity to methanol. The effect of nitroarene codeposition on selectivity to aromatic compounds is pronounced (Figure

Figure 3. Response to a 0.5-μL injection of acetonitrile on SGFET coated with various PP: (a) PP/4-nitrotoluene; (b) PP/2-nitrotoluene; (c) PP/3-nitrotoluene; (d) PP from acetonitrile; (e) PP from methanol; (f) PP/toluene; (g) PP/nitrobenzene
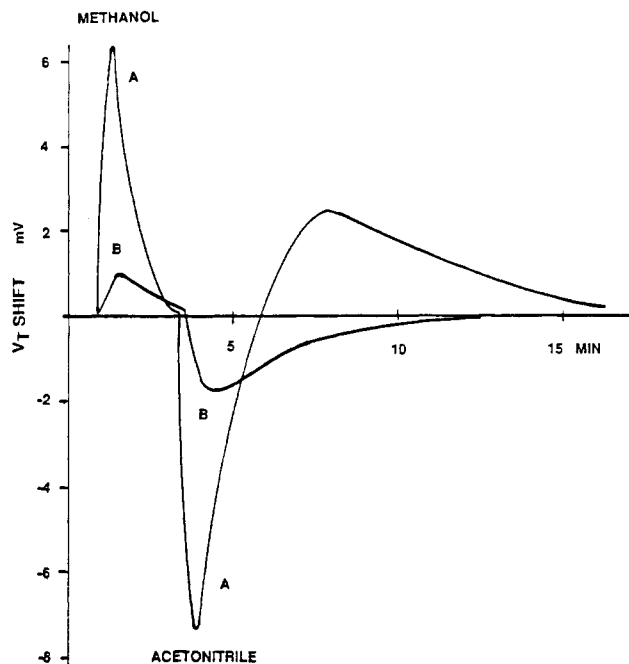
Figure 4. Response of polypyrrole deposited from (A) methanol or (B) acetonitrile to injection of 5 μL of methanol:acetonitrile mixture (1:10 molar ratio). Nitrogen flow was 24 mL min^{-1}; V_{DS} = 4.0 V; I_{DS} = 350 μA.

Figure 2. MSRS spectra resulting from reductive and oxidative pulsing for (– – –) PP, (•••) PP/2-nitrotoluene, (–•–•) PP/3-nitrotoluene, (–••–••) PP/4-nitrotoluene, and (——) PP/nitrobenzene (spectrum "nb" is that of solution nitrobenzene radical anion): (a) initial reduction, base potential –0.60 V, pulse height –1.80 V; (b) oxidation, base potential –0.60 V, pulse height +1.80 V; (c) reduction spectra recorded after film oxidation, base potential –0.60 V, pulse height –1.80 V. Sensitivity in (a) and (c) is five times that of (b). Other parameters are given in the text.
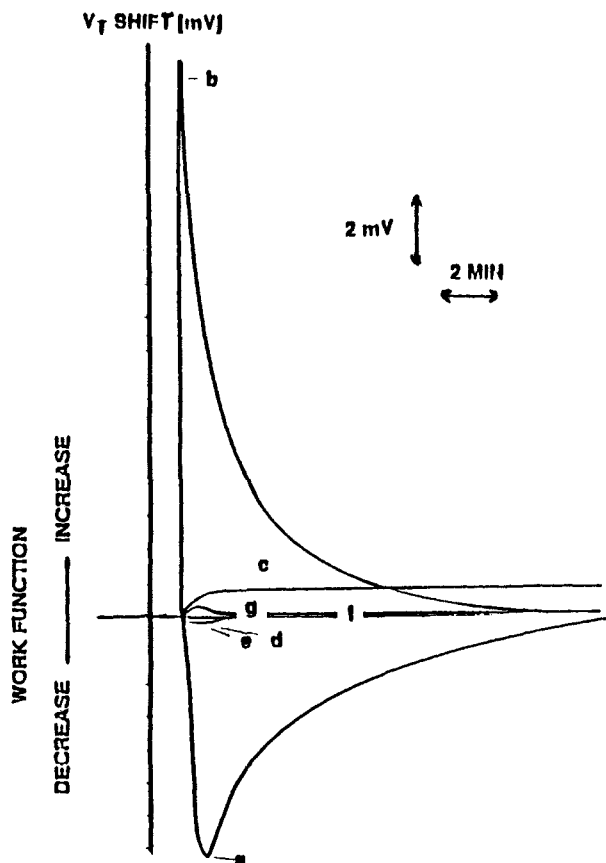
5). While there is no sensitivity to toluene of transistors with PP deposited from methanol, acetonitrile, or acetonitrile/1 M toluene solutions, both 2-nitro- and 4-nitrotoluene PP give a strong, reversible response to toluene, while PP/3-nitrotoluene yields only a weak, irreversible response.

Figure 5. Response to a 2-μL injection of toluene on SGFET coated with various PP: (a) PP/4-nitrotoluene; (b) PP/2-nitrotoluene; (c) PP/3-nitrotoluene; (d) PP from acetonitrile; (e) PP from methanol; (f) PP/toluene; (g) PP/nitrobenzene.
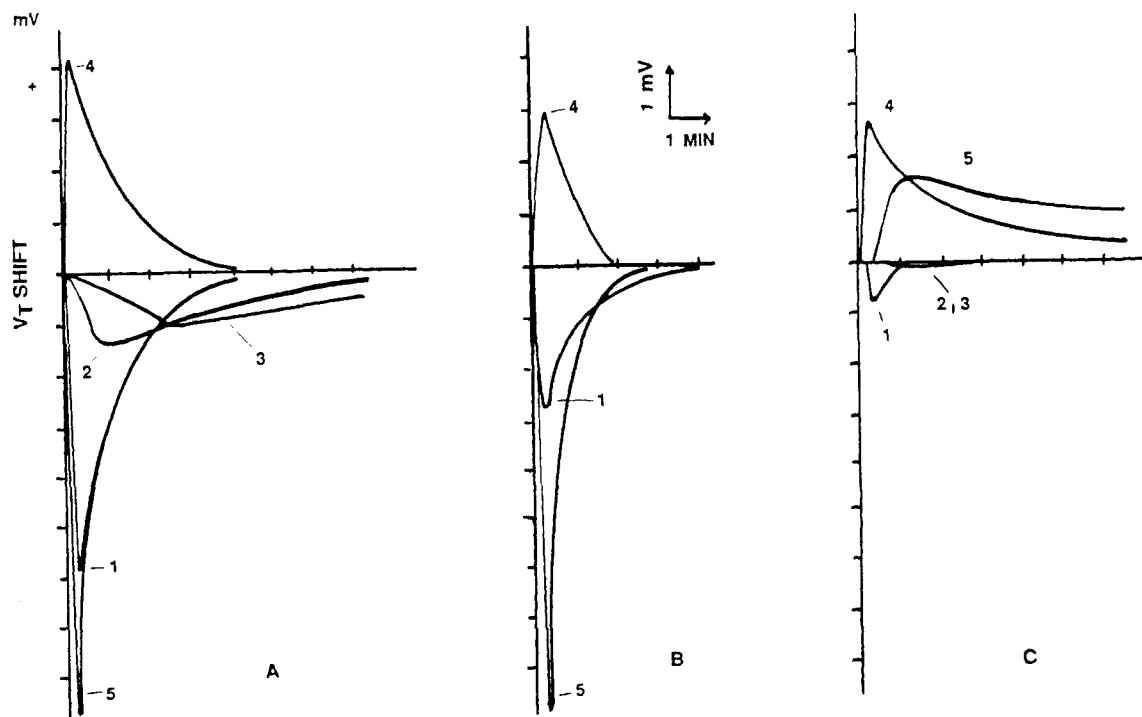
Response of SGFET coated with PP/nitrobenzene depends on the electrochemical history of this material; the responses were reproducible for different films made under identical conditions. There was some degradation in response after repeated cycling. The PP/nitrobenzene deposited with the final potential at ±0 V (Figure 6A) yields a response to water, to alcohols, and to the aromatics. Reduced material (Figure 6B,C) shows a much lower response to aromatics and a lower and inverted response to water. This behavior can be explained by the gradual loss of nitrobenzene from the PP matrix upon reduction of the nitro group. As expected none of the tested coatings listed in Table I responded to aliphatic hydrocarbons or to cyclohexane.
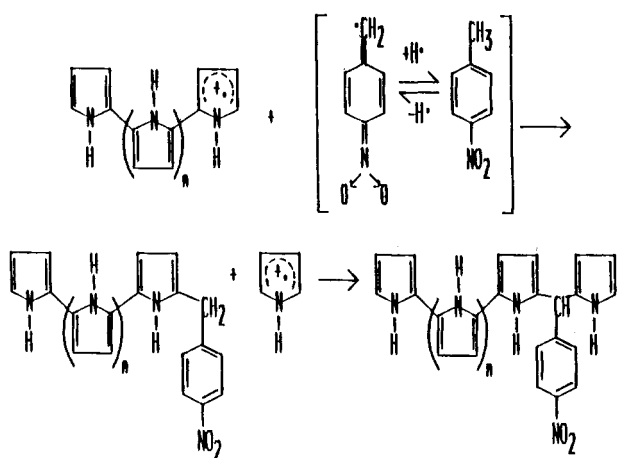
DISCUSSION

Because of the complex geometry of the transistor gate (Pt mesh) and the resulting nonhomogeneous electric field in the gap, no absolute equilibrium measurements have been attempted in this work. However, the rapid return of the signal to the base line (Figures 3–6) following the passage of the concentration impulse is a clear indication of the reversibility of these interactions. The exception seems to be the response of PP/3-nitrotoluene to toluene which is irreversible (curve c in Figure 5).

In this group of sensors, PP is used only as a binding matrix, but we see that the chemical selectivity is achieved by incorporation of additional functional groups. As has been observed previously, SGFETs with PP layers respond to alcohols and water. This selectivity is undoubtedly related to the tendency of pyrrole to hydrogen bond (12). Not surprisingly, all transistors investigated in this study have shown a response to aliphatic alcohols and to water. The fact that the response to water was stronger when the electrodeposition of PP was carried out from methanol rather than from acetonitrile (Figure 4) indicates that solvation during the polymerization may have left the final polymer with "solvent footprints" which made it an entropically more favorable binder for the organic substrate of similar shape. This may be termed a solvent-induced template effect similar to one proposed, for example, by Shea and Dougherty (13) for template-mediated synthesis. In this context the PP may not be an optimum matrix because of its high crystallinity (14). Electropolymerization of PP in the presence of 1 M toluene

Figure 6. Response of SGFET coated with PP/nitrobenzene in acetonitrile to injection of 0.5 μL of (1) acetonitrile, (2) benzene, (3) toluene, (4) and methanol; (5) and 0.1 μL of water: (A) at final deposition potential ±0 V; (B) after reduction at –1.0 V for 10 min; (C) after repeated cycling between ±0 and –2.5 V.

Scheme I

Figure 7. Band diagram illustrating observed electronic transitions in polypyrrole films.

has not resulted in enhanced sensitivity to toluene (Figure 5f). This addition of acetonitrile vapor is consistent with the negative ΔV_T of PP deposited from acetonitrile solution (relative to PP deposited from methanol). The origin of this shift is again presumably in the N–π or N–H interactions between acetonitrile and PP.

The copolymerization of PP with nitrotoluenes produced a remarkably strong shift in the threshold voltage (Table I) of the final material as compared to the plain PP (+6.787 V for 2-nitrotoluene, +8.984 V for 3-nitrotoluene, and +7.784 V for 4-nitrotoluene). Such large shifts can be explained only by copolymerization of pyrrole with nitrotoluene and formation of a substantially different material with much higher electron affinity. The likely mechanism for this reaction involves the nitrotoluyl radical, analogous to the reaction between pyrrole and the benzyl radical (15). (See Scheme I.)

The presence of incorporated nitroarene has been confirmed by cyclic voltammetry (Figure 1) and by spectroelectrochemistry (Figure 2). On the other hand, nitrobenzene, which cannot readily copolymerize with PP, was found to bind only loosely, presumably as a charge-transfer complex with the neutral PP. Upon oxidation of the matrix the nitrobenzene is rapidly lost by diffusion with concomitant loss of sensitivity to aromatic analytes (Figure 6). The sensitivity to aromatic hydrocarbons and the total lack of sensitivity to cyclohexane are probably due to the N–π interactions of the former with the nitroarene moiety within the PP/nitrotoluene copolymer. The polarity of the response, i.e., induced increase or decrease of the electron affinity, is difficult to explain at present and is the subject of further study.

The electropolymerization of PP is a convenient yet chemically complicated process in which different materials are formed depending on the current density and on the solvent and anion present in the solution during electrolysis (16). Unfortunately the mesh structure of our suspended gate transistor does not allow us to control the current density such that the exact PP film thickness or a film of uniform chemical composition could be produced.

The MSRS spectra clearly indicate the incorporation of nitrotoluenes into polypyrrole. The difference spectra of the three nitrotoluene/polypyrrole aggregates resemble the spectra obtained from polypyrrole electrodeposited in the absence of any nitroarene (Figure 2). As a result of the initial film reduction (Figure 2a), a positive peak at 440 nm, corresponding to the interband transition in neutral polypyrrole (7) (Figure 7), appears in the difference spectra of the three nitrotoluene/polypyrrole films as well as in the spectrum of the polypyrrole film itself. Also, a broad negative peak at around 550 nm, due to the reduced form of the polymer (Figure 7), is seen for all five films. During film oxidation, a very broad positive peak with a maximum near 600 nm is observed for
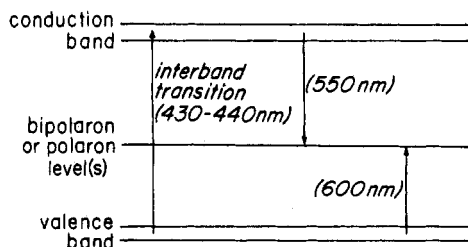
all five films, along with a shoulder near 430 nm. The shoulder corresponds to interband transitions seen above during film reduction. The broad, humped peak, with its maximum around 600 nm, is due to transitions in the neutral polymer matrix as well (Figure 7) and probably owes its broadness and structure to the presence of oligomers of varying chain length. It has yet to be shown unequivocally whether the intermediate band in PP is a polaron or a bipolaron. Spectral dependence on chain length has been noted before for polypyrrole (17) and in polyparaphenylene (18).

The magnitude of the peak at 600 nm (Figure 2b) is larger then expected due to the fact that the oxidized form of the polymer is conductive and therefore acts optically more like a metal. Since what is recorded is a difference spectrum, the small absorbances in the visible range due to the neutral species translate into bands of large magnitude when compared with the near zero absorbance occurring at the electrode surface of the oxidized form of the film. The 430–440-nm band is depressed relative to the 580–620-nm band since the oxidized form of the polymer absorbed to some extent at these higher energies (17). This is indicated in the difference spectra. No peak due to the oxidized form appears at any wavelength. However, a small contribution to the absorbance in the violet cut-off region due to transitions in the oxidized species cancels to some extent the band due to the neutral form of PP in the 430–440-nm region.

The difference spectrum obtained during the *initial* reduction of PP/nitrobenzene (recorded *prior* to any oxidation) shows the only optical anomaly (Figure 2a); a negative peak around 400 nm is observed, with thee positive peak due to the neutral form of the polymer matrix absent. No such phenomenon appears in the MSRS spectra of the other four polymer films; the other four films show a positive peak in the 440-nm region and a broad negative peak in the 550-nm region. The spectrum of nitrobenzene radical anion in acetonitrite (Figure 2a, insert) shows a broad peak with a minimum near where the interband transition in the neutral form of PP occurs. It is presumed that the signal due to nitrobenzene radical anion formed during the reduction of surface adsorbed nitrobenzene overwhelms the absorbance due to the interband transition, which is opposite in sign. This accounts for the apparent negative peak at 395 nm and the absence of a positive peak at 440 nm; both nitrobenzene radical and neutral PP absorb in thee same wavelength region, and a competition is established which results in the more complex difference spectrum (Figure 2a). The resulting difference spectrum for PP/nitrobenzene is a sum of the spectrum for PP alone and the nitrobenzene difference spectrum. A second reduction (Figure 2c) following oxidation (Figure 2b) results in thee disappearance of the nitrobenzene anion radical peak which is negative in sign, with the appearance of some positive $\Delta R/R$ contribution from the 430–440-nm interband transition band of the neutral species. The spectrum from PP/nitrobenzene (Figure 2c) is now similar in appearance to the spectra obtained for the other four films. This is evidence that the charge-transfer complex between nitrobenzene and PP postulated previously is probably destroyed when the film is

oxidized. Here, spectral information complements voltammetric data (Figure 1), suggesting that nitrobenzene is not incorporated into the polymer during electropolymerization, whereas the three nitrotoluene species do indeed copolymerize with pyrrole to form the PP matrix.

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Hydrogen Ion Selective Microelectrode Prepared by Modifying an Electrode with Polymers

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A new type of potentiometric pH sensor which consists of a graphite microelectrode coated with the two kinds of polymeric films in a bilayer state is introduced. The pH sensor does not contain an inner standard solution layer between the electrode substrate and the film. The electrode surfaces are coated with a film of poly(pyrenamine) and then with a film of the neutral carrier by use of the hydrogen ion exchanger. The sensor has rapid response of the electromotive force to changes in the pH, high ion selectivity with respect to Na$^+$, K$^+$, and Ca^{2+}, and insensitivity to O$_2$ gas, characteristics similar to those reported for conventional pH glass–membrane electrodes. The satisfactory responses for hydrogen ion are still observed in serum.

Recently, polymeric films have been used as modifiers of electrode surfaces (1-6) and electrode modification with functional polymers is promising in its potential applications to analytical sensors. Several papers report the use of a polymer-modified electrode as a potentiometric sensor, especially as a pH sensor (7-10). In the case of pH sensors, the acid–base properties of films electrochemically deposited on the electrode surface are expected to impart a pH response to the electrode substrate. In most cases, however, the hydrogen ion selectivity of the sensor is depressed due to interaction of other redox systems at the electrode surface or changes of the surface during use.

The glass–membrane electrode is the most widely used pH sensor and it has an internal filling solution between the electrode substrate and pH-sensitive membrane. However, in the design of a microsensor, the filling solution layer is sometimes troublesome. Therefore the construction of pH sensors still needs improvement for special needs. The coated wire electrode, which consists of a conductor directly coated with an ion-responsive membrane (usually based on poly(vinyl chloride)), has been used as a sensor and has no internal aqueous filling solution. However, coated wire electrodes, which are simpler to construct, are less stable than glass electrodes and they are sensitive to various chemical interferences.

In order to improve the properties of coated wire electrodes, we have attempted to fix the thermodynamics at the underlying solid electrode composed of solid/membrane/solution by modifying the electrode substrate with a thin film. The thin film that has been used is electrochemically active and the volume concentration of the electroactive redox site is of the order of 1 M. Therefore, it is expected that the redox couples in the thin film actually determine the potential level of the electrode surface. With a naked electrode an equilib-