

# A Study of Polyaniline Microtubules: Toward Superior Transducing Abilities

S. Sukeerthi<sup>†</sup> and A. Q. Contractor<sup>\*</sup>

Department of Chemistry, Indian Institute of Technology, Powai, Mumbai 400 076, India

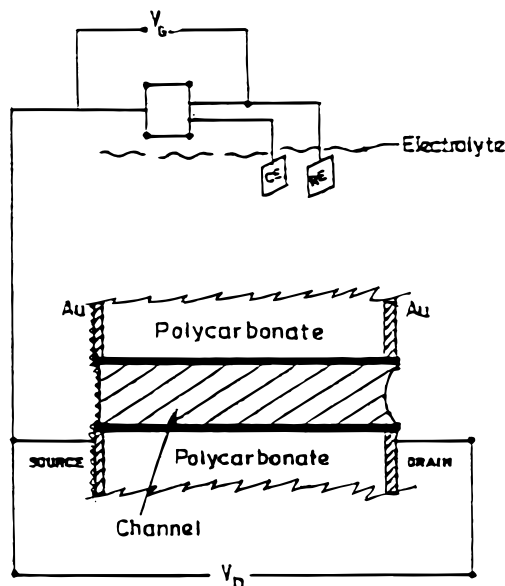
Received February 23, 1998. Revised Manuscript Received June 11, 1998

Polyaniline grown into pores of polycarbonate membrane has been shown to behave like a microelectrochemical transistor. The nature of the polycarbonate membrane results in a fraction of the polyaniline growing in an ordered and compact fashion along the walls of the pore. The switching properties of polyaniline grown into such pores changes significantly when the polycarbonate membrane is treated with a surfactant like Triton X 100. The polyaniline obtained in this case is largely disordered and open, with room for changes in conformation. This disordered material therefore shows larger changes in conductivity, about a factor of  $10^2$  larger, than the ordered material on switching from insulating to conducting state.

## Introduction

By combining microfabrication techniques and derivatization of electrode surfaces with redox active materials, it has been possible to assemble structured,  $\mu$  scale, electroactive systems that perform useful functions based on the chemical sensitivity of the system components.<sup>1–5</sup> A large number of redox-active organic polymers have been shown to exhibit widely varying conductivities depending on their oxidation state. The first demonstrated microelectrochemical device employed arrays of microelectrodes derivatized with polypyrrole and poly(*N*-methyl)pyrrole<sup>6,7</sup> as the channel material. Since then, efforts have been concentrated on polyaniline<sup>8</sup> and poly-3-methylthiophene,<sup>9</sup> which exhibit superior operating characteristics such as switching time, power amplification, and durability. All these polymers are insulating when reduced and conducting when partially oxidized. In some cases, the difference in conductivities in the oxidized and in the reduced states can vary by as much as 8 orders of magnitude.<sup>7</sup>

In our laboratory, we have carried out in situ conductance measurements based on the same concept as above with various electrode configurations. Such measurements were first carried out with Pt twin wire



A MICROTUBULE TRANSISTOR

**Figure 1.** Microtubule transistor of polyaniline. The two gold-coated faces of the membrane act as source and drain, respectively; polyaniline deposited in the tubular pore acts as the channel material. Key: RE, reference electrode; CE, counter electrode;  $V_g$ , gate voltage;  $I_d$ , drain current;  $V_d$ , drain voltage.

electrodes by Gholamian et al.<sup>10</sup> Similar measurements were carried out with interdigitated microelectrodes (IMPs).<sup>11</sup> Since fabrication of these devices was expensive and time-consuming, we looked for an alternative approach. Martin et al.<sup>12–22</sup> have synthesized polypyr-

<sup>†</sup> Current address: 277 Watts Hall, Department of Materials Sciences, Ohio State University, 2041 College Road, Columbus, OH 43210.

<sup>\*</sup> To whom correspondence should be addressed. E-mail: aliasgar@ether.chem.iitb.ernet.in.

- (1) Chidsey, C. E. D.; Murray, R. W. *Science* **1986**, *231*, 25.
- (2) Wrighton, M. S. *Science* **1986**, *231*, 32.
- (3) Natan, M. J.; Mallouk, T. E.; Wrighton, M. S. *J. Phys. Chem.* **1987**, *91*, 948.
- (4) Murray, R. W.; Ewing, A. G.; Drust, R. A. *Anal. Chem.* **1987**, *59*, 379A.
- (5) Smith, D. K.; Lane, G. A.; Wrighton, M. S. *J. Phys. Chem.* **1988**, *92*, 2616.
- (6) Kittelson, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 7389.
- (7) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.
- (8) Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* **1986**, *90*, 6674.
- (9) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.

(10) Gholamian, M.; Suresh Kumar, T. N.; Contractor, A. Q. *Proc. Ind. Acad. Sci.* **1986**, *97*, 457.

(11) Sangodkar, H.; Sukeerthi, S.; Lal, R.; Srinivasa, R. S.; Contractor, A. Q. *Anal. Chem.* **1996**, *68*, 779.

(12) Martin, C. R. *Acc. Chem. Res.* **1995**, *28*, 61.

(13) Martin, C. R. *Science* **1994**, *266*, 1961.

(14) Liang, W.; Martin, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 9666.

(15) Parthasarathy, R. V.; Martin, C. R. *Chem. Mater.* **1994**, *6*, 1627.

**Table 1. Comparison of Resistance/Pore ( $\Omega$ ) at  $-0.2$  V and  $+0.3$  V vs SCE for Polyaniline Tubules 1.2 and 0.2  $\mu\text{m}$  in Diameter (Mean and Standard Deviation (S. D.) Are Also Listed)**

S no.	0.2 $\mu\text{m}$ @ $-0.2$ V vs SCE	0.2 $\mu\text{m}$ @ $+0.3$ V vs SCE	1.2 $\mu\text{m}$ @ $-0.2$ V vs SCE	1.2 $\mu\text{m}$ @ $+0.3$ V vs SCE
Condition A				
1	$6.7 \times 10^9$	$1.3 \times 10^5$	$8.6 \times 10^9$	$9.8 \times 10^5$
2	$6.0 \times 10^9$	$1.8 \times 10^5$	$12.1 \times 10^9$	$11.2 \times 10^5$
3	$9.1 \times 10^9$	$4.4 \times 10^5$	$8.0 \times 10^9$	$18.4 \times 10^5$
4	$12.2 \times 10^9$	$8.2 \times 10^5$	$18.0 \times 10^9$	$9.0 \times 10^5$
5	$1.3 \times 10^{10}$	$1.1 \times 10^5$	$2.2 \times 10^{10}$	$2.2 \times 10^6$
6	$1.1 \times 10^{10}$	$1.4 \times 10^5$	$2.4 \times 10^{10}$	$2.5 \times 10^6$
mean	$9.66 \times 10^9$	$3.03 \times 10^5$	$1.54 \times 10^{10}$	$1.59 \times 10^6$
SD	$2.9 \times 10^9$	$2.81 \times 10^5$	$6.86 \times 10^9$	$6.82 \times 10^5$
Condition B				
1	$4.0 \times 10^{14}$	$1.3 \times 10^8$	$3.2 \times 10^{12}$	$4.0 \times 10^5$
2	$3.2 \times 10^{14}$	$1.3 \times 10^8$	$4.0 \times 10^{12}$	$7.8 \times 10^5$
3	$7.9 \times 10^{14}$	$1.3 \times 10^8$	$7.9 \times 10^{12}$	$1.1 \times 10^6$
4	$5.0 \times 10^{14}$	$1.3 \times 10^8$	$5.0 \times 10^{12}$	$1.6 \times 10^6$
5	$1.0 \times 10^{15}$	$1.3 \times 10^8$	$1.0 \times 10^{13}$	$3.2 \times 10^6$
6	$1.6 \times 10^{15}$	$1.3 \times 10^8$	$1.6 \times 10^{13}$	$5.0 \times 10^6$
mean	$7.68 \times 10^{14}$	$1.30 \times 10^8$	$7.68 \times 10^{12}$	$2.01 \times 10^6$
SD	$4.80 \times 10^{14}$	0.0	$4.80 \times 10^{12}$	$1.75 \times 10^6$

role and polyaniline in the micron- and submicron-sized tubular pores of isoporous membranes. In this paper, we describe an adaptation of this synthesis strategy to fabricate simple microelectrochemical transistors with good switching properties. The changes accompanying switching have been observed by carrying out in situ conductivity measurements and in situ UV-vis experiments. This phenomenon has been interpreted and understood in terms of the concept of secondary doping proposed by MacDiarmid et al.,<sup>23–28</sup> in which they describe the polymer to be in a “compact coil” state when it is insulating and in an “expanded coil” conformation in its conducting state. They have also investigated the effect of disorder on the dc conductivity of polyaniline.<sup>29–31</sup> The extent of order/disorder in the present study was investigated by PIRAS.

### Experimental Section

Polycarbonate membranes were obtained from Millipore Inc. Studies were carried out with two sets of membranes having pores of 1.2 and 0.2  $\mu\text{m}$  diameter, respectively, and membrane thickness of 10  $\mu\text{m}$ . Pore densities were calculated with the

help of scanning electron micrographs of 1.2 and 0.2  $\mu\text{m}$  membranes. Around six pictures of various regions of the membrane were taken, and the number of pores/cm<sup>2</sup> was calculated. The pore densities were  $9.1 \times 10^6$  pores/cm<sup>2</sup> for the membranes with 1.2  $\mu\text{m}$  pores and  $4.3 \times 10^8$  pores/cm<sup>2</sup> for the membranes with 0.2  $\mu\text{m}$  pores.

The membranes were coated with Au (thickness 1000 Å) on both sides using a model no. 15F6 HINDHIVAC vacuum evaporation system. The gold films acted as electrodes during polymerization and subsequently as the “source” and “drain” of the electrochemical transistor. Aniline was AR grade and was distilled and stored under nitrogen. Polyaniline was grown electrochemically on the gold-coated faces, and polymerization was continued until the two faces were bridged by the polymer growing into the pores, thereby acting as the channel material (Figure 1). Polyaniline was grown into the membrane pores during electropolymerization by potentiodynamic cycling at 50 mV/s between  $-0.2$  and  $+0.8$  V vs SCE using an EG & G PARC model 362 potentiostat/galvanostat. Electropolymerization was performed under the following three sets of conditions: (A) from a monomer solution of 0.1 M aniline in 0.5 M H<sub>2</sub>SO<sub>4</sub> onto a gold-coated membrane, (B) from the above solution onto a gold-coated membrane treated with 0.01% Triton-X 100 for 20 min prior to polymerization, and (C) from a monomer solution containing 0.01% Triton X 100 onto a gold-coated membrane without pretreatment.

In situ resistance measurements were made with the help of a model AFRDE4 PINE bipotentiostat. The measurement of resistance was made by holding one face of the membrane at a fixed potential,  $V_g$ , and the other face at  $V_g + 20$  mV. The potential difference developed between the electrodes was  $V_d$  ( $= 20$  mV), and the current flowing as a result of the potential difference was  $I_d$ . The gate voltage,  $V_g$ , was varied between  $-0.2$  and  $+0.5$  V vs SCE. The corresponding  $I_d$  was recorded with the help of a Linsies XY recorder.

**Spectroscopic Characterization.** Polarized IR absorption measurements were carried out with a Nicolet Magna FTIR spectrophotometer. Spectra of polyaniline were obtained by subtracting spectra of the gold coated polycarbonate (Au-PC) membrane from the polyaniline Au-PC membrane. Prior to the deposition of polyaniline, the Au-PC membrane was mounted in the sample holder, and background spectra were obtained for parallel and perpendicular polarizations. These spectra showed strong absorption bands of polycarbonate. Polyaniline tubules were then deposited into the membrane electrochemically as described above. The membrane was again placed in the sample holder, and spectra were once again recorded for the two polarizations. Such measurements were carried out for polymers grown under conditions A–C.

In situ UV-vis spectra of polyaniline in polycarbonate membrane were recorded on a Shimadzu 2100 UV spectro-

(16) Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. R. *Chem. Mater.* **1991**, *3*, 960.

(17) Dyke, L. S.; Martin, C. R. *Langmuir* **1990**, *6*, 1118.

(18) Brumlik, C. J.; Martin, C. R. *J. Am. Chem. Soc.* **1991**, *113*, 3174.

(19) Lakshmi, B. B.; Dorhout, P. K.; Martin, C. R. *Nature* **1997**, *388*, 758.

(20) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739.

(21) Parthasarathy, R.; Martin, C. R. *Nature* **1994**, *369*, 298.

(22) Cai, Z.; Martin, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4138.

(23) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1995**, *69*, 85.

(24) Avlyanov, J. K.; Min, Y.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1995**, *72*, 65.

(25) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1995**, *69*, 85.

(26) Joo, J.; Prigodin, V. N.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1994**, *50*, 12226.

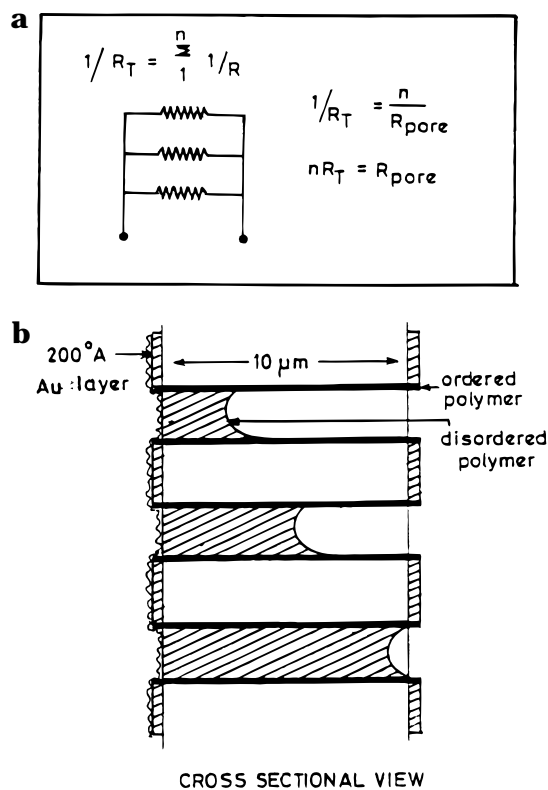
(27) McCall, R. P.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1994**, *50*, 5094.

(28) Joo, J.; Oblakowski, Z.; Du, G.; Pouget, J. P.; Oh, E. J.; Wesinger, J. M.; Min, Y.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1994**, *49*, 2977.

(29) Jozefowicz, M. E.; Laueranne, R.; Javadi, H. H. S.; Epstein, A. J.; Pouget, J. P.; Tang, X.; MacDiarmid, A. G. *Phys. Rev. B* **1989**, *39*, 12958.

(30) Kohlman, R. S.; Joo, J.; Min, Y. G.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. Lett.* **1996**, *77*, 2766.

(31) Kohlman, R. S.; Zibold, A.; Tanner, D. B.; Ilhas, G. G.; Ishiguro, T.; Min, Y. G.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. Lett.* **1997**, *78*, 3915.

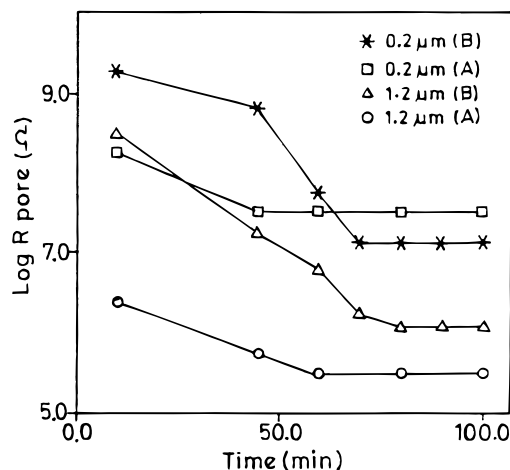


**Figure 2.** (a) Schematic representation of the equivalent conductance path through the polyaniline-filled membrane. The resistance of polyaniline deposited in each pore is represented by a resistance  $R_{\text{pore}}$ ,  $n$  is the number of pores. (b) Schematic cross-sectional view of the polyaniline-coated PC membrane. The gold layer on the left was the working electrode during electropolymerization.

photometer. Background correction was made by keeping gold-coated polycarbonate membranes of the same pore diameter in the reference holder. Polyaniline was grown electrochemically on the membrane, and spectra were then recorded in situ at various potentials. Potential was controlled with an EG & G PARC model 362 potentiostat/galvanostat.

## Results and Discussion

In situ resistance measurements were carried out with polyaniline-coated polycarbonate membrane hav-

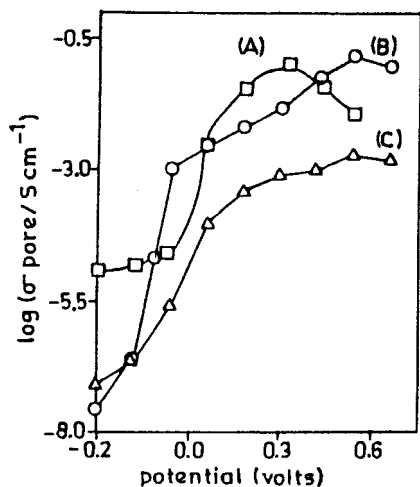


**Figure 3.** Dependence of pore resistance as a function of polymerization time. The resistance was recorded at  $-0.2$  V vs SCE. Polymerization conditions A and B are as described in the text.

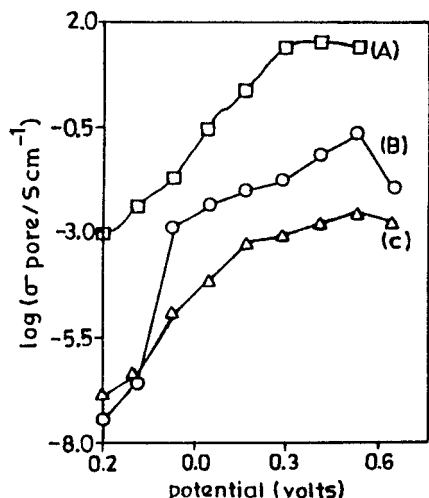
ing pores of diameters 1.2 and  $0.2 \mu\text{m}$ , respectively. The membranes used are isoporous. These membranes have pore walls that are hydrophobic in nature; therefore, the polymer preferentially nucleates and grows on the pore walls according to Martin et al.<sup>12</sup> By controlling the polymerization time, tubules with thin and thick walls could be produced. A completely plugged pore has polyaniline growing in an ordered fashion along the walls of the pore due to the hydrophobic nature of the wall/water interface and disordered polyaniline growing away from the walls. The change in resistance on going from the most resistive state to the most conductive state for a  $1.2 \mu\text{m}$  membrane coated with PANI is of the order of  $10^5$ . Treatment of the membrane with a nonionic surfactant like Triton-X 100 prior to polymerization modifies the nature of the wall/water interface. Adsorption of the surfactant on the polycarbonate surface inhibits the growth of polyaniline along the pore wall, and the polyaniline chains now tend to grow into the solution phase. A number of similar experiments with the PANI-coated polycarbonate membranes were carried out under identical conditions. The reproducibility of resistance values obtained from measurement to measurement were scrutinized carefully. Table 1

**Table 2. Polymerization Charges**

20-min Duration			
1.2 μm (A)	1.2 μm (B)	0.2 μm (A)	0.2 μm (B)
48.5	32.4	84.9	56.4
46.6	33.1	85.2	56.8
48.8	32.8	84.6	55.4
47.9	33.4	83.8	57.3
45.9	34.7	84.7	56.0
44.4	31.8	85.2	55.8
mean = 47.02	mean = 33.03	mean = 84.77	mean = 56.28
SD = 1.698	SD = 0.989	SD = 0.520	SD = 0.694
"Plugging the Pores Completely"			
1.2 μm (A) (60 min)	1.2 μm (B) (90 min)	0.2 μm (A) (45 min)	0.2 μm (B) (80 min)
146.8	114.5	166.8	136.4
145.5	115.3	169.3	135.0
149.2	112.5	172.2	135.4
151.1	112.0	168.2	139.5
148.8	114.3	166.0	142.3
151.6	112.9	170.9	140.0
mean = 148.28	mean = 113.50	mean = 168.90	mean = 138.64
SD = 2.17	SD = 1.27	SD = 2.38	SD = 2.92



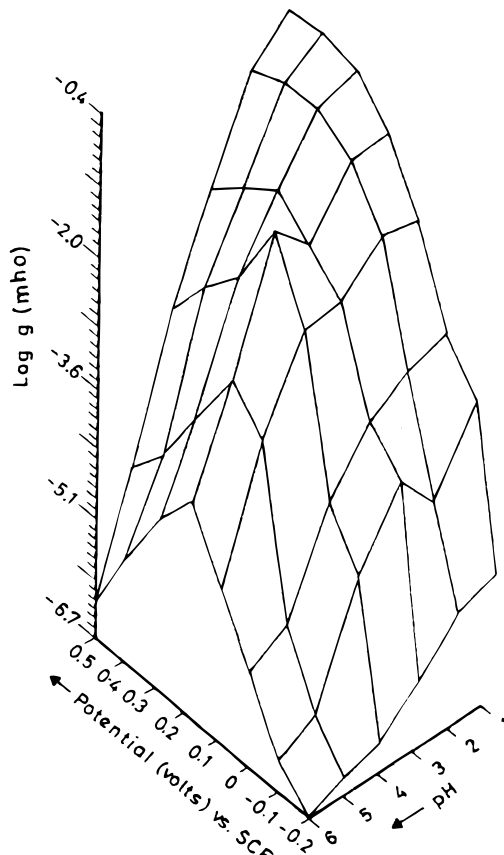
**Figure 4.** Change in conductivity with potential for a 1.2  $\mu\text{m}$  polyaniline tubule. The polymer was grown under conditions A–C.



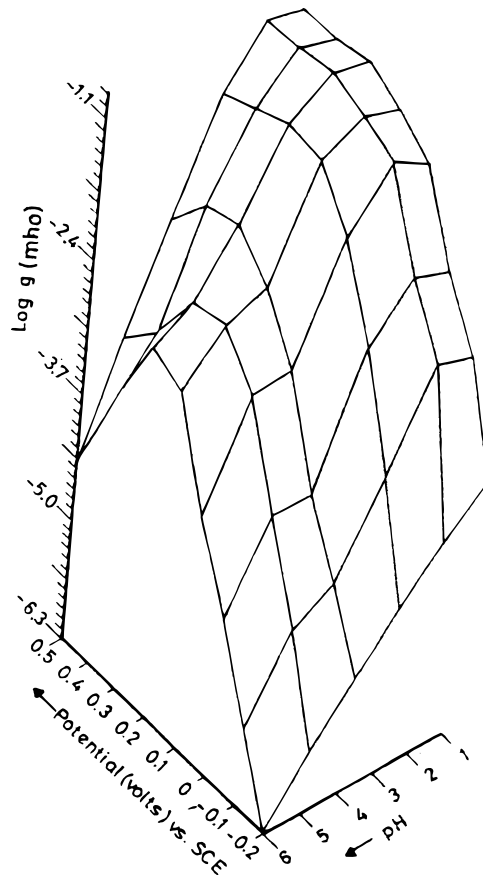
**Figure 5.** Change in conductivity with potential for a 0.2  $\mu\text{m}$  polyaniline tubule. The polymer was grown under conditions A–C.

shows the values of  $R_{\text{pore}}$  at  $-0.2$  and  $+0.3$  V vs SCE obtained for polyaniline-coated 1.2 and 0.2  $\mu\text{m}$  membranes. The resistance per pore,  $R_{\text{pore}}$ , was calculated from the total measured resistance by assuming that all channels are identical and represent parallel resistances as illustrated in Figure 2a. This is true once all pores are completely plugged, and the device resistance does not change any further with increasing polymerization time.

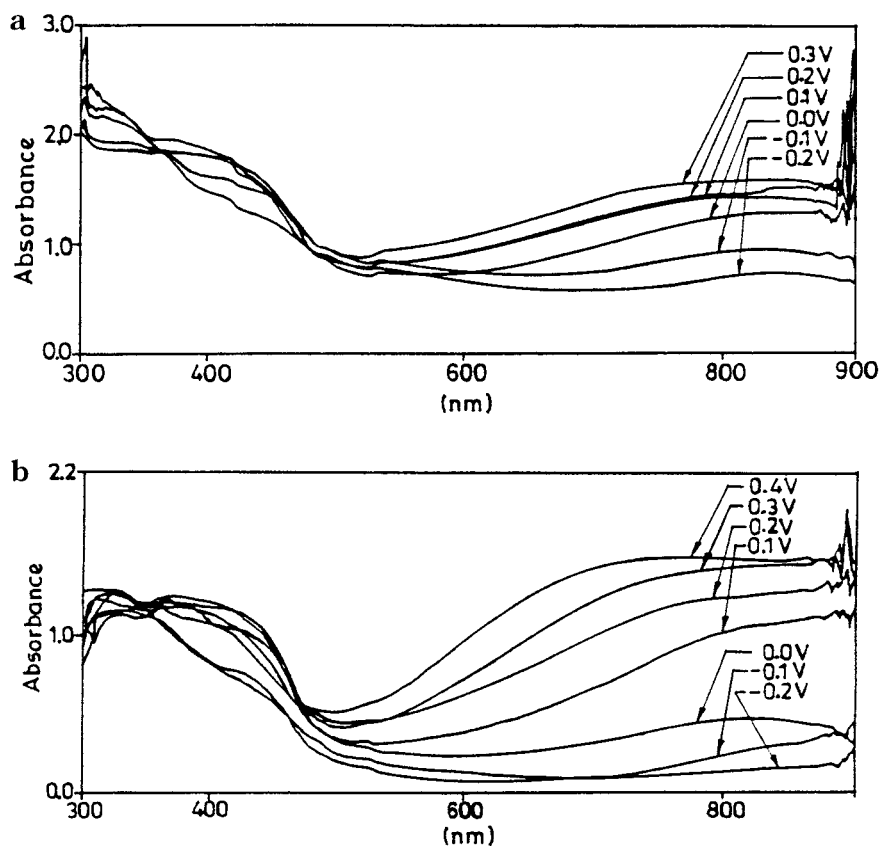
In situ conductivity measurements were made with completely “plugged” pores. The time taken to plug pores was dependent on the pore diameter and the conditions of polymerization. Figure 3 shows the dependence of  $R_{\text{pore}}$  as a function of polymerization time. The 0.2  $\mu\text{m}$  pore was plugged in about 45 min and the 1.2  $\mu\text{m}$  in about 60 min when the polymerization was carried out under condition A. The duration for completely plugging the pore was enhanced if the polymerization was carried out under condition B. The 1.2  $\mu\text{m}$  pore was plugged in about 90 min, whereas the 0.2  $\mu\text{m}$  pore was plugged in 80 min. This observation is supported by the finding reported by Nishizawa et al.<sup>32</sup> that polyaniline grows along a hydrophobic surface at



**Figure 6.** Three-dimensional surface “state diagram” of 0.2  $\mu\text{m}$  polyaniline tubules showing changes in conductance with potential and pH.



**Figure 7.** Three-dimensional surface “state diagram” of 1.2  $\mu\text{m}$  polyaniline tubules showing changes in conductance with potential and pH.



**Figure 8.** (a) In situ UV-vis spectra of polyaniline tubules of diameter  $0.2 \mu\text{m}$ . The polymer was synthesized under condition A. (b) In situ UV-vis spectra of polyaniline tubules of diameter  $0.2 \mu\text{m}$ . The polymer was synthesized under condition B.

a much faster rate than into the aqueous solution. This observation is further substantiated by comparing the polymerization charges for polyaniline grown under conditions A and B in both  $1.2$  and  $0.2 \mu\text{m}$  pores.

In the completely plugged pore, in which the polymer is grown under condition A, there is a fraction of ordered polymer along the walls of the pore, whereas polyaniline grown under condition B is largely disordered. This phenomenon is illustrated schematically in Figure 2b. A comparison of conductivity of these "plugged pores" was made. The variation of conductance/pore with potential for completely plugged pores is shown in Figures 4 and 5. Changes are observed in the absolute conductances of the ordered system, i.e., conductances of polymers grown under condition A are higher than those of polymer tubules grown under condition B and also that the absolute conductances of the  $0.2 \mu\text{m}$  tubules are higher than the  $1.2 \mu\text{m}$  tubules. The disordered tubules show around  $10^7$ -fold change in conductivity on switching of polyaniline, whereas the ordered polymeric tubules show only around  $10^5$ -fold change. The polymeric tubules grown under condition C show intermediate values. The above observations lead to two important conclusions. First, the ordered tubules show large values of conductivities. This is probably because the polymer grown along the pore walls is tightly packed and ordered to a large extent and, hence, has fewer kinks or defects along the polymer backbone, which makes electron conduction along the chains easier. The smaller diameter pore has a larger

proportion of ordered polymer; hence, it exhibits larger absolute values of conductivities than the  $1.2 \mu\text{m}$  pore. Second, the disordered polymeric tubules in both  $1.2$  and  $0.2 \mu\text{m}$  pores show a larger transitions in conductivity on switching. This may be due to the fact that polymer chains are less tightly packed and therefore are free to undergo changes in conformation. Therefore, on applying more positive potentials, the influx of counterions into the polymer mass is easier in this case. However, the absolute values of conductivity are lower because the polymer chains being disordered have a larger number of kinks and defects along the backbone; therefore, charge carrier mobility along the chains is hindered.

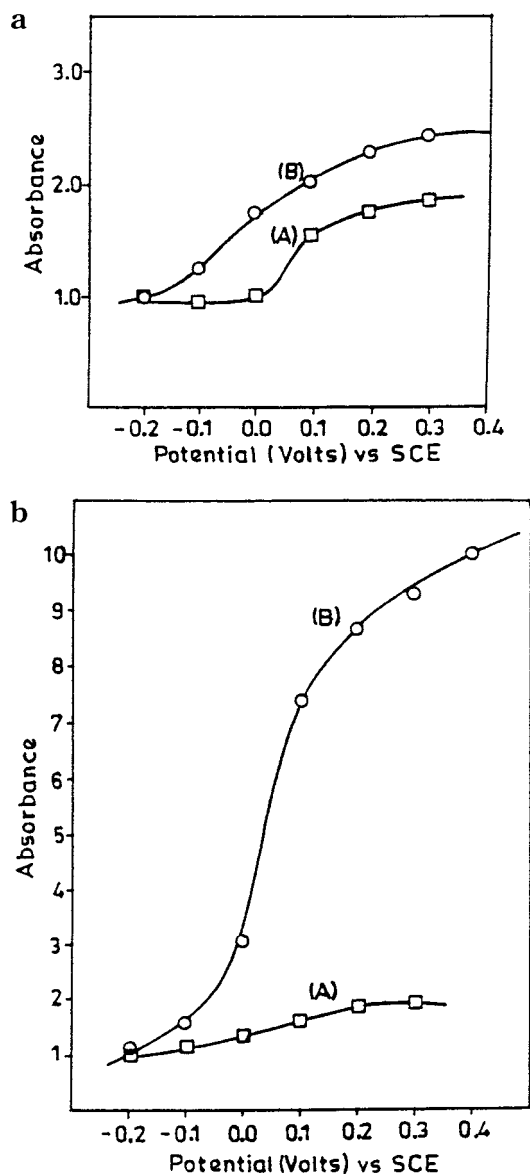
A study of variation of polyaniline conductivity with pH and potentials has been carried out for PANI grown in polycarbonate membranes of  $1.2$  and  $0.2 \mu\text{m}$  pore diameters, respectively. The resistance of the polymer increases with pH in agreement with the earlier reports.<sup>33,34</sup> There is a slow evolution in the resistance electrochemical potential behavior with the resistance minimum becoming sharper at higher pH. These data were used to generate a conductance surface "state-diagram" as shown in Figures 6 and 7. These state-diagrams have been used as an aid in developing sensors for various biomolecules.

The above conclusions were further supported by data from in situ UV-vis studies. Spectra were recorded

(32) Nishizawa, M.; Miwa, Y.; Matsue, T.; Uchida, I. *J. Electrochem. Soc.* **1993**, *140* (6), 1050.

(33) Travers, J. P.; Nechtschein, M. *Mol. Cryst. Liq. Cryst.* **1987**, *21*, 135.

(34) Ochmanska, J.; Pickup, P. G. *J. Electroanal. Chem.* **1991**, *297*, 211.



**Figure 9.** (a) Normalized absorbance–potential plot for 1.2  $\mu\text{m}$  ordered polyaniline tubules (polymer synthesized by procedure A) and disordered polymer tubules (synthesized by procedure B). (b) Normalized absorbance–potential plot for 0.2  $\mu\text{m}$  ordered polyaniline tubules (polymer synthesized by procedure A) and disordered polymer tubules (synthesized by procedure B).

with polyaniline<sup>35–37</sup> grown in both ordered and disordered fashion, using conditions A and B, respectively. Figure 8a,b shows the UV–vis spectra of polyaniline tubules of diameter 0.2  $\mu\text{m}$  for ordered and disordered systems, respectively. Since changes in conformation are associated with transitions in the longer wavelength region, the absorbance of the 800 nm band was monitored. This band is followed by a free carrier tail consistent with the delocalization of electrons in the polaron band promoted by “straightening out” of the polymer chain as its ordered structure becomes more

expanded with concomitant reduction in defects along the polymer backbone.<sup>24–30</sup> In the case of the surfactant-treated membranes, the polyaniline–solvent interaction becomes stronger than the polyaniline–pore wall interactions, leading to a more disordered polymer film. The varying extent of order/disorder provided a very interesting correlation in conductivity and UV–vis absorption spectra of polyaniline formed in these pores. The absorbance vs potential profile at 800 nm correlates very well with the conductivity behavior as shown in Figure 9a,b. The ordered systems show less changes in absorbance, whereas the disordered systems show large changes with potential, as may be expected since both absorption and conductivity changes are associated with conformational changes.

The extent of order/disorder was also investigated by polarized infrared absorption spectroscopy (PIRAS). The ratio of absorbances in the parallel and perpendicular planes of polarization, called the “dichroic ratio”, was calculated for the absorption bands at 1500  $\text{cm}^{-1}$  corresponding to C–C stretching and C–H bending and at 1600  $\text{cm}^{-1}$  due to C–C stretching of the benzene ring.<sup>38</sup> The data are presented in Table 3. The first layer of polyaniline chain that deposits on the pore walls is influenced by the oriented polycarbonate chains of the wall. As the polymer film grows thicker, the influence of the pore walls diminishes, resulting in a disordered central core. On treatment with the surfactant, the nature of the wall/water interface is altered and polymer chains are not aligned anymore. The dichroic ratios indicate that as we go from highly ordered (pores having polymer synthesized by method A) to totally disordered (solution cast free-standing films of polyaniline) the ratio increase and approach 1.

These membrane-based transistors have been used for making sensors for various biomolecules. In this context, the switching in electronic conductivity of the polymer films is relevant. It has been found that the sensitivities of sensors made from disordered polymer are significantly higher.<sup>39</sup> These studies are being reported separately.

## Conclusions

It has been demonstrated that microelectrochemical transistors can be fabricated on isoporous membranes. The membrane-based devices are a good alternative to the silicon-based devices. These are easy to fabricate and inexpensive; therefore, can be used as disposables. These devices based on conducting polymers have tremendous potential to serve as sensors for various substrates by immobilizing the appropriate molecular recognition element into the polymer matrix.

It is found that the device characteristics are influenced by the extent of order/disorder in the polymer matrix. Order is introduced by the nature of the interface between the membrane material and the polymerization medium. This interface can be altered to promote the growth of disordered polymer, which shows a larger change in conductance between the

(35) Cushman, R. J.; McManus, P. M.; Yang, S. C. *J. Electroanal. Chem.* **1987**, 219, 335.

(36) McManus, P. M.; Yang, S. C.; Cushman, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1556.

(37) McManus, P. M.; Cushman, R. J.; Yang, S. C. *J. Phys. Chem.* **1987**, 91, 744.

(38) Quillard, S.; Loran, G.; Lefrant, S.; MacDiarmid, A. G. *Phys. Rev. B* **1994**, 50 (17), 12496.

(39) Sukeerthi, S. Ph.D. Thesis, IIT, Bombay, 1997.

**Table 3. Dichroic Ratios<sup>a</sup>**

wavenumber (cm <sup>-1</sup> )	bare gold-coated PC membrane	ordered polymer synthesized according to A	disordered polymer synthesized according to C	disordered polymer synthesized according to B	cast films of chemically synthesized polymer
			0.2 $\mu$ m Tubules		
1500	0.30	0.12	0.38	1.166	0.93
1600	0.21	0.12	0.21	0.67	0.97
			1.2 $\mu$ m Tubules		
1500	0.42	0.089	0.42	0.74	0.93
1600	0.38	0.173	0.44	0.53	0.97

<sup>a</sup> Electropolymerization was performed under the following three sets of conditions: (A) from a monomer solution of 0.1 M aniline in 0.5 M H<sub>2</sub>SO<sub>4</sub> onto a gold-coated membrane, (B) from the above solution onto a membrane treated with 0.01% Triton-X 100 prior to polymerization, and (C) from a monomer solution containing 0.01% Triton X 100 onto a gold-coated membrane without pretreatment.

insulating and conducting states. Such a polymer film should be preferable for transducer applications such as biosensors and molecular switches.

**Acknowledgment.** It is a pleasure to acknowledge the numerous discussions with Drs. S. S. Talwar, R. Lal,

and R. S. Srinivasa that helped in bringing clarity to our understanding of this system. We are grateful to RSIC, IIT, Mumbai, for help in obtaining the polarized IR data. S.S. acknowledges the receipt of a CSIR SRF.

CM980096K