

AD-A158 854 POLY-3-METHYLTHIOPHENE COATED ELECTRODES OPTICAL AND
ELECTRICAL PROPERTIES. (U) MASSACHUSETTS INST OF TECH
CAMBRIDGE DEPT OF CHEMISTRY J W THACKERAY ET AL
UNCLASSIFIED 15 AUG 85 ONR-TR-6 N00014-84-K-0291 F/G 9/1

POLY-3-METHYLTHIOPHENE COATED ELECTRODES OPTICAL AND
ELECTRICAL PROPERTIES (U) MASSACHUSETTS INST OF TECH
CAMBRIDGE DEPT OF CHEMISTRY J W THACKERAY ET AL
15 AUG 85 ONR-TR-6 N00014-84-K-0291 F/G 9/1

1/1

UNCLASSIFIED

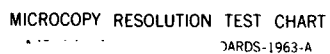
15 AUG 85 ONR-TR-6 N00014-84-K-0291

F/G 9/1

NL

END

© 2000 John Wiley & Sons, Inc.



MICROCOPY RESOLUTION TEST CHART
NBS-1963-A

[Prepared for publication as an Article in the Journal
of Physical Chemistry]

Poly-3-Methylthiophene Coated Electrodes: Optical And Electrical Properties As
A Function Of Redox Potential And Amplification Of Electrical And Chemical
Signals Using Poly-3-Methylthiophene-Based Microelectrochemical Transistors

James W. Thackeray, Henry S. White, Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

AD-A158 854

DTIC
ELECTE
AUG 29 1985
S D
G

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

* Address correspondence to this author.

85 8 20 104

DTIC FILE COPY

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR TR6	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Poly-3-Methylthiophene Coated Electrodes: Optical & Electrical Properties as a Function of Redox Potential and Amplification of Electrical & Chem. Signals.....		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) James W. Thackeray, Henry S. White, Mark S. Wrighton		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139		8. CONTRACT OR GRANT NUMBER(s) N00014-84-K-0291
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Work Unit # 202-261
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE August 15, 1985
		13. NUMBER OF PAGES 18
		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public release; reproduction is permitted for any purpose of The United States Government; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Distribution of this document is unlimited.		
18. SUPPLEMENTARY NOTES Prepared for Publication in the <u>Journal of Physical Chemistry</u>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) conducting polymers, microelectrochemistry, molecular electronics modified electrodes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Attached		

Abstract

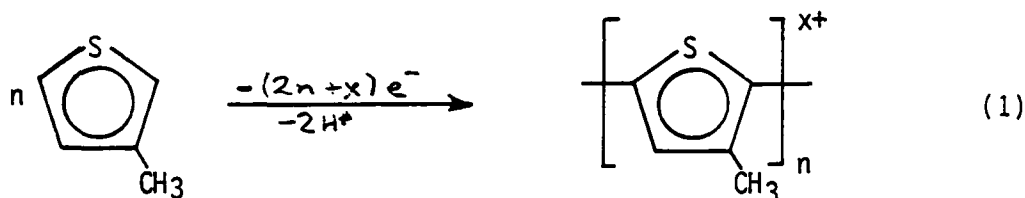
Optical and electrical properties of anodically grown poly-3-methylthiophene are reported as a function of redox potential in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$. Poly-3-methylthiophene can be grown by the oxidation of 3-methylthiophene and deposited onto Au or Pt electrode surfaces. The poly-3-methylthiophene can be used to "connect" two or more closely spaced ($1.2 \text{ } \mu\text{m}$) microelectrodes ($2.4 \text{ } \mu\text{m}$ wide \times $50 \text{ } \mu\text{m}$ long \times $0.1 \text{ } \mu\text{m}$ thick) of a microelectrode array fabricated using conventional microfabrication techniques. A pair of poly-3-methylthiophene-connected microelectrodes can function as a transistor where one of the electrodes is regarded as P_{source} and the other as P_{drain} with the source being referenced to the solution as a gate. The poly-3-methylthiophene is the analogue of the channel of a solid state field effect transistor, since its conductivity changes by $>10^8$ depending on the potential. Large optical (300-800 nm) and electrical changes for the poly-3-methylthiophene occur between $\sim +0.3 \text{ V}$ and $\sim +0.8 \text{ V}$ vs. SCE. The reduced material has an absorption maximum at 490 nm and the oxidized material has an absorption maximum at 750 nm. The optical density changes parallel the resistance changes that occur as the potential of the polymer changes between $\sim +0.3$ and $\sim +0.8 \text{ V}$ vs. SCE. The charging of a $1.5 \text{ } \mu\text{m}$ thick film of poly-3-methylthiophene involves $\sim 10^4$ times more charge per unit of projected area than a smooth Pt electrode, consistent with a large effective internal surface area for the conducting polymer. The resistance of poly-3-methylthiophene falls by greater than eight orders of magnitude upon oxidation, and the drain current, I_D , vs. gate voltage, V_G , at a fixed drain potential, V_D , of a poly-3-methylthiophene-based transistor gives a transconductance, $\partial I_D / \partial V_G$, of 120 mS/mm of channel width, competitive with high quality Si MOSFET devices. Power amplification of a factor of about

1000 is possible at frequencies of 10 Hz. In aqueous 0.1 M NaClO_4 /0.05 M NaH_2PO_4 (pH = 5.3) the poly-3-methylthiophene-based transistor is durable and the resistance can be varied by $>10^5$ by variation in potential. A poly-3-methylthiophene-based electrochemical transistor placed in the effluent stream of a high pressure liquid chromatograph reproducibly turns on or off in response to a chemical oxidant (IrCl_6^{2-}) or reductant ($\text{Fe}(\text{CN})_6^{4-}$), respectively, introduced into the system via an automatic injector. The microelectrochemical transistor responds to $<10^{-9}$ moles of oxidant injected. Since only $\sim 8 \times 10^{-5}\%$ of the injected material passes by the transistor, the amount of oxidant to which the device responds is $<10^{-15}$ moles.

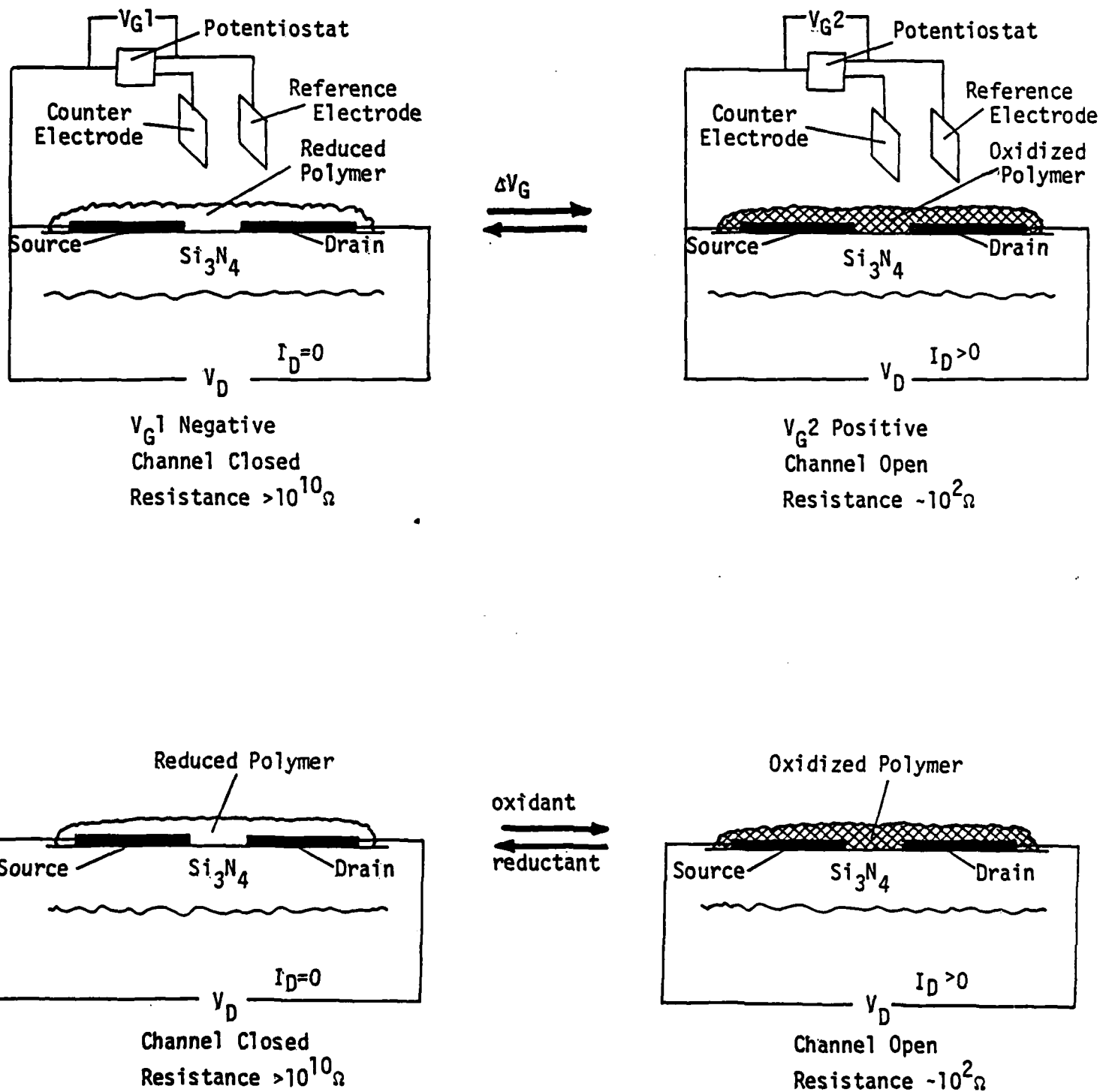
Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
AI	AI



We wish to report some new phenomena associated with the reversible oxidation of poly-3-methylthiophene. In particular, we report the change in resistance and optical spectral changes in the 300-800 nm wavelength range as a function of potential for an electrode-confined film of polymer derived from the oxidation of 3-methylthiophene, equation (1).¹ The poly-3-methylthiophene



can be deposited onto an array of closely spaced (1.2 μm) microelectrodes (2.4 μm wide x 50 μm long x 0.1 μm thick) in a controlled manner, as recently described for polypyrrole,^{2,3} polyaniline⁴, polyvinylferrocene,⁵ and a polyviologen.⁵ Two or more of the eight microelectrodes of an array can be connected by the poly-3-methylthiophene, allowing the demonstration of microelectrochemical transistors, Scheme I. Compared to previously reported molecular materials used to fabricate molecule-based transistors,²⁻⁴ the poly-3-methylthiophene has the advantage of being durable in aqueous solution.¹ In addition, the transconductance of poly-3-methylthiophene-based devices is superior to any molecule-based device²⁻⁴ and is similar to that for state-of-the-art Si MOSFET devices.⁶ These favorable properties make the poly-3-methylthiophene-based devices promising as chemical sensors and experiments have been carried out to show that poly-3-methylthiophene-based transistors can be reproducibly turned on or off by oxidants or reductants, respectively. Thus, electrical, Scheme Ia, or chemical, Scheme Ib, signals can be amplified by poly-3-methylthiophene-based transistors.



Scheme I. Poly-3-methylthiophene-based microelectrochemical transistors for the amplification of (a) electrical or (b) chemical signals.

Experimental Section

Preparation of Microelectrode Arrays. The microelectrode arrays used in this work are those previously described.⁵ Each chip consists of eight Au microelectrodes with contact leads and pads. The design is one which places the contact pads on one side of the chip⁵ (rather than symmetrically disposed about the chip)²⁻⁴ so that the contact leads, pads, and external leads can be easily insulated by hand with ordinary epoxy. The microelectrode arrays are fabricated on 2" diameter single crystal Si wafers on which is grown a 1 μm SiO_2 layer which is then capped with a 0.43 μm thick Si_3N_4 layer. The Au microelectrodes are deposited on top of the Si_3N_4 and are thus insulated from the Si. The eight Au microelectrodes are 50 μm long x 2.4 μm wide x 0.1 μm thick and are separated from each other by 1.2 μm . After packaging into electrode assemblies the arrays are typically "cleaned" by scanning the potential of all eight electrodes to a value sufficiently negative to evolve H_2 from aqueous 0.1 M K_2HPO_4 . The microelectrodes are then "tested" by examining their electrochemical behavior in aqueous 0.1 M LiCl containing 5 mM $\text{Ru}(\text{NH}_3)_6^{3+}$. A good array shows the same response for each of the eight microelectrodes: a well-developed current-voltage curve at 50 mV/s for reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ characteristic of microelectrodes.^{5,7}

Chemicals. The CH_3CN was HPLC grade and used as received from commercial sources. The 3-methylthiophene was obtained commercially and distilled prior to use. The electrolytes were $[\text{n-Bu}_4\text{N}]\text{ClO}_4$ (Southwestern) for CH_3CN solvent or LiClO_4 (Alfa) for H_2O solvent. Redox reagents $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, $\text{K}_4\text{Fe}(\text{CN})_6$, and K_2IrCl_6 were used as received from commercial sources.

Equipment. UV-VIS spectra were recorded using a Hewlett-Packard Model 8451-A Diode Array spectrometer in the 300-800 nm region or a Cary 17 for near-IR measurements. The SEM photographs were obtained using a Cambridge Mark 2A stereoscanning electron microscope with resolution of 20 nm. Electrochemical

equipment included a PAR Model 173/175 Potentiostat/Programmer for the characterization of macroscopic electrodes and a Pine Instruments RDE-4 Bipotentiostat for the characterization of microelectrodes. A Houston 2000 X-Y recorder or an oscilloscope was used to record data using the PAR equipment and a Kipp and Zonen BD 91 X-Y-Y' recorder was used for recording characteristics of the microelectrodes when the Pine Instruments equipment was used. A Hewlett Packard Model 1084-b high pressure liquid chromatograph was used as the system to generate reproducible chemical signals to be detected by a poly-3-methylthiophene-based transistor.

Electrochemical Growth of Poly-3-Methylthiophene. Poly-3-methylthiophene can be grown onto electrode surfaces by oxidizing 3-methylthiophene in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ solution. The typical procedure involves cycling (200 mV/s) the potential of an electrode to be derivatized between 0.0 V and +1.8 V vs. SCE in the presence of 50 mM 3-methylthiophene. The deposited polymer exhibits a cyclic voltammetry wave with a peak at $\sim +0.7 \text{ V}$ vs. SCE. The cyclic voltammetry wave at $\sim +0.7 \text{ V}$ vs. SCE can be used to gauge the amount of polymer deposited. In derivatizing a microelectrode array, only those electrodes to be derivatized were cycled and those not to be derivatized were held at a negative potential, -1.0 V vs. SCE, to preclude growth of the poly-3-methylthiophene.

Thickness Measurements. Thickness measurements of poly-3-methylthiophene, made by oxidizing 3-methylthiophene on Au films coated onto microscope slides, were made using a Sloan Dektak Surface Profiling System. The "step" from the Au to the polymer was defined by using Apiezon M grease to insulate a section of the Au electrode surface during deposition of the poly-3-methylthiophene. After the anodic growth of polymer onto the grease-free region of the Au the grease was removed with CH_2Cl_2 . The Au (0.5 μm thick) was coated onto the microscope slides by evaporation.

Optical Spectral Measurements. Poly-3-methylthiophene was deposited onto partially optically transparent Au electrodes. The Au electrodes were prepared by evaporating Au onto microscope slides. The typical Au thickness was $\sim 0.5 \mu\text{m}$ which is sufficiently transparent, yet sufficiently conducting, for the UV-VIS spectroelectrochemistry of the deposited polymer films. The optical spectra vs. potential were recorded using the Hewlett Packard Diode Array spectrometer or the Cary 17.

Chemical Stimulation of Poly-3-methylthiophene-Based Transistors.

Reproducible and repetitive chemical signals were delivered to poly-3-methylthiophene-based transistors by placing the transistor in the effluent stream of the Hewlett Packard HPLC. The automatic injector was used to inject samples of oxidant, $\text{K}_2[\text{IrCl}_6]$, or reductant, $\text{K}_4[\text{Fe}(\text{CN})_6]$, into a stream of aqueous electrolyte. A macroscopic Pt electrode was used as an indicator electrode to determine the solution potentials vs. time. To determine the amount of IrCl_6^{2-} actually reaching the surface of the microelectrode array two of the "naked" (non-derivatized) microelectrodes were used as an indicator electrode. The naked electrodes were held at a potential where IrCl_6^{2-} would be reduced to IrCl_6^{3-} , 0.0 V vs. SCE and the integral of the current-time plot following an injection of IrCl_6^{2-} was used to determine the number of oxidizing equivalents that comprise a given chemical signal. The poly-3-methylthiophene-based transistor was typically operated at a drain potential, V_D , Scheme Ib, of 0.1 V.

Results and Discussion

Derivatization of Macroscopic Electrodes with Anodically Grown Films of Poly-3-Methylthiophene: Charging and Optical Spectra vs. Potential. The "capacity" and optical properties of poly-3-methylthiophene deposited onto macroscopic Au electrodes have been determined in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$, in order to fully understand the operations of the poly-3-methylthiophene-based microelectrochemical transistors described below. The optical spectral changes in the near-UV/VIS (300-800) are substantial when the potential is varied between $\sim +0.3$ and $+1.0 \text{ V vs SCE}$, Figure 1. For the range of potentials and wavelengths shown it would appear that there are no spectral changes for potentials beyond $\sim +0.8 \text{ V vs. SCE}$. However, examination of the near-IR region, 800-1500 nm, shows that additional spectral changes do occur as the electrode potential is moved positive of $+0.8 \text{ V vs SCE}$. The near-IR spectral changes do not reveal well-defined absorption bands. Rather, more positive potentials yield increased absorption in the near-IR over a broad wavelength region.

That optical spectral changes occur in the near IR with additional movement in potential beyond $\sim 0.8 \text{ V vs. SCE}$ is in accord with the finding that charge can be withdrawn from the poly-3-methylthiophene beyond $+0.8 \text{ V vs. SCE}$. In fact, as the data in Figure 2 show, the total charge withdrawn from the polymer as a function of potential appears to be linear with potential in a potential regime where the visible region of the optical spectrum is nearly constant, Figure 1. Other workers have reported⁸ that polythiophene undergoes near-IR spectral changes at positive potentials, as found here for the poly-3-methylthiophene.

The data in Figure 2 show that the poly-3-methylthiophene has a remarkable capacitance: $1.9 \times 10^2 \text{ F/cm}^2$. The inset in Figure 2 shows a

linear plot of mF/cm^2 vs. polymer thickness; the slope of the straight line gives the capacitance of the film. The individual data points for the various thicknesses shown in the inset of Figure 2 are from the slopes of the plots of charge vs. potential for potentials more positive than +0.5 V vs. SCE where the charge vs. potential appears to be quite linear. For comparison, the charge vs. potential for a smooth Pt electrode is included in Figure 2. This charge is the double layer charging associated with the metallic electrode and the capacitance is $\sim 10 \mu\text{F}$. Obviously, the poly-3-methylthiophene-coated electrodes have a large capacitance, and in the potential regime more positive than +0.5 V vs. SCE the poly-3-methylthiophene appears to behave as a "metallic" electrode of very high internal surface area. Note that the $1.5 \mu\text{m}$ thick poly-3-methylthiophene films give a capacity some 10^4 times greater than a smooth Pt electrode. Such a high capacity has been noted previously for polypyrrole.^{9,10}

The large capacitance of the poly-3-methylthiophene or polypyrrole is not unique: any redox polymer will have a fairly large capacitance, since the redox polymers such as polyvinylferrocene or polyviologen have of the order of $1\text{--}3$ moles of monomer units per cubic centimeter of polymer.^{11,12} This means that for a one-electron change per monomer the capacity is $\sim 1\text{--}3 \times 10^2 \text{ F/cm}^3$. What is different about the poly-3-methylthiophene (and presumably other "conducting" polymers) is that there is a more or less well-defined and wide potential regime where the charge vs. potential is linear. For polyvinylferrocene and polyviologen the charge vs. potential would not be linear over a wide potential regime, because the redox subunits comprising the polymer do not interact strongly and charge is added or extracted from the polymer at potentials within $\sim 100 \text{ mV}$ of the formal potential. For poly-3-methylthiophene the potential region between $\sim +0.1$ and $+0.5 \text{ V vs. SCE}$

is a regime that can be regarded as analogous to the polyviologen or polyvinylferrocene behavior, but as the potential is moved more positive the poly-3-methylthiophene becomes "metallic" in behavior.¹³

The conclusion that the poly-3-methylthiophene becomes metallic for potentials positive of +0.5 V vs. SCE is supported by the dramatic changes in conductivity upon electrochemical oxidation, vide infra. In the sense that a linear plot of charge vs. potential could be obtained, a polymer having a variety of redox subunits with closely spaced redox potentials could be regarded as "metallic". For example, a polymer derived from ring-substituted derivatives of vinylferrocene could have a linear charge vs. potential plot for a wide potential range. However, unlike the poly-3-methylthiophene such a polymer would not be expected to have high conductivity because the individual redox subunits do not interact strongly: the polyvinylferrocene^{5,11} has a "conductivity" some 10^6 times lower than poly-3-methylthiophene.¹ The point is that polyvinylferrocene, and other conventional redox polymers, do have some features in common with conducting polymers, but there are important differences as well.

The potential of poly-3-methylthiophene cannot be moved positive without limit. Extraction of charge makes the polymer more and more positively charged and more and more reactive in electrolyte solutions. In dry CH_3CN the films remain durable to at least +1.4 V vs. SCE. In H_2O , potentials positive of $\sim +0.8$ V vs SCE lead to decomposition. Thus, extracting charge from "metallic" poly-3-methylthiophene brings about chemical changes, as well as the near-IR spectral changes noted above. In another vein, the amount of charge that can be withdrawn from a conducting polymer without adversely affecting the conductivity will be a function of the polymer: polyaniline⁴ shows a relatively small potential region of high conductivity compared to

polypyrrole.^{2,3,14} Further, the change in conductivity with "doping" level can be a function of the polymer.¹⁵ With respect to microelectrochemical devices, such as the transistors, it is these variations in properties that can be exploited to demonstrate unique device characteristics.

Derivatization of Microelectrodes With Poly-3-methylthiophene. Electrochemical oxidation of 3-methylthiophene at Au microelectrodes results in the deposition of electroactive poly-3-methylthiophene that behaves as it does when deposited onto macroscopic Au or Pt electrodes. As for other polymers deposited onto microelectrode arrays,^{2-5,7} the poly-3-methylthiophene can be deposited onto the array in a controlled fashion. In particular, the amount of polymer deposited and the electrode derivatized can be controlled. The amount of polymer deposited can be controlled by control of the charge passed to form the deposited polymer. Derivatization of a particular microelectrode of a set of closely-spaced (1.2 μm separation) microelectrodes is possible by holding electrodes not to be derivatized at -1.0 V vs. SCE while oxidizing 3-methylthiophene at the electrode(s) to be derivatized. Holding an electrode at a negative potential actively "discourages" growth of the poly-3-methylthiophene. Figure 3 illustrates an eight electrode array with three adjacent microelectrodes purposely derivatized with poly-3-methylthiophene with the remaining five electrodes kept free of polymer.

The poly-3-methylthiophene derivatized microelectrode arrays have been fully characterized by electrochemical methods in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ and to a lesser extent in various aqueous media. Figure 4 shows cyclic voltammograms as a function of sweep rate for a pair of adjacent, derivatized microelectrodes in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$. Note that the essential features of the cyclic voltammetry waves for the derivatized microelectrodes are the

same as for macroscopic electrodes derivatized with poly-3-methylthiophene. It is also important to note that a microelectrode not purposely derivatized, but adjacent to the ones derivatized, shows little or no electrochemical response characteristic of the immobilized poly-3-methylthiophene. Thus, electrochemical characterization, which can be useful to detect very small amounts (~monolayer) of redox active material, substantiates SEM characterization, Figure 3, of the derivatized microelectrode arrays that shows that the electrodes can be modified in a controlled fashion.

Cyclic voltammetry can be used to establish that two (or more) microelectrodes can be connected with poly-3-methylthiophene. Figure 4 illustrates data for two adjacent microelectrodes. The key fact is that the cyclic voltammograms (at any sweep rate shown) have the same area when electrode A alone is driven, when electrode B alone is driven, and when electrodes A and B are driven together. These facts are consistent with the conclusion that electrodes A and B are connected by polymer and that all of the polymer is accessible by addressing A or by addressing B or by addressing A and B together. The fact that A alone and B alone give the same cyclic voltammogram could be consistent with the conclusion that electrodes A and B are derivatized with the same amount of polymer but are not connected with polymer. However, if this conclusion were true the cyclic voltammogram from driving A and B together would have an area equal to the area from A alone plus the area from B alone. The data show that when A and B are driven together as one electrode the area of the cyclic voltammogram is the same as for A alone or B alone. Thus, for the range of sweep rates illustrated in Figure 4 the pair of microelectrodes are connected by the immobilized poly-3-methylthiophene. We find that the minimum amount of poly-3-methylthiophene that can be used to connect two of the microelectrodes is associated with a cyclic voltammogram

that has an area corresponding to 10^{-8} C in a cyclic sweep between 0.0 and +0.8 V vs. SCE.

Resistance of Poly-3-methylthiophene As Function of Potential. The fact that cyclic voltammetry shows that poly-3-methylthiophene connects two microelectrodes at sweep rates up to 500 mV/s is consistent with the relatively high conductivity of poly-3-methylthiophene. At such a sweep rate an ordinary (low conductivity) redox polymer, such as polyvinylferrocene,¹¹ that connects the microelectrodes at slow sweep rates (5 mV/s) would behave as if the two microelectrodes are not connected: the area of the cyclic voltammogram for A and B driven together would be the sum of the areas for A and B alone.^{5,7} Steady state current-voltage data can be used to show directly that charge can be passed from one microelectrode to a second, polymer-connected, microelectrode to assess the resistance of the polymer as a function of the potential of the polymer. Figure 5 gives representative data from studies of a pair of microelectrodes connected by poly-3-methylthiophene: the resistance between the two connected microelectrodes declines by greater than eight orders of magnitude upon a change in potential from 0.0 V to +0.8 V vs. SCE.

The experimental data summarized by Figure 5 have been obtained as reported previously for polypyrrole- and polyaniline-connected microelectrodes:²⁻⁴ one of the two microelectrodes is held at a potential, V_G , and the potential of the other microelectrode is moved linearly in time ± 20 mV (V_D) around the fixed potential of the first, while monitoring the current, I_D , that passes between the two microelectrodes. The current that passes through one electrode/polymer interface is equal in magnitude, but opposite in sign, to the current that passes through the other electrode/polymer interface. The resistance is taken to be the slope of the I_D vs. V_D plot at $V_D = 0$. Control experiments have been done with adjacent, non-derivatized

microelectrodes and the "resistance" between them in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ is observed to be $>10^{10} \Omega$. The data in Figure 5 are for $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$. Similar resistance vs. potential plots are found in $\text{H}_2\text{O}/\text{electrolyte}$ ($\text{pH} = 1$ to 9 ; $0.1 \text{ M } \text{LiClO}_4$ or $0.1 \text{ M } \text{NaClO}_4$ or $0.1 \text{ M } \text{HClO}_4$), except the maximum resistance at -0.2 V vs. SCE only goes to $\sim 8 \times 10^7 \Omega$. The minimum resistance is nearly the same as in CH_3CN , $\sim 10^2 \Omega$. The potential "window" for non-Faradaic processes in H_2O is significantly less than in CH_3CN , owing to the small decomposition potential for H_2O . It is important to note that the resistance changes in the poly-3-methylthiophene with variation in potential are reversible, provided the positive limit is less than $+1.4 \text{ V}$ vs. SCE in CH_3CN and less than $+0.8 \text{ V}$ vs. SCE in H_2O . More positive potentials give irreversible oxidative degradation of the polymer.

The poly-3-methylthiophene has a maximum conductivity that is superior (by about one order of magnitude) to that found for polypyrrole^{2,3} in $\text{CH}_3\text{CN}/[\text{n-Bu}_4\text{N}]\text{ClO}_4$ and the total change in conductivity is larger for a given potential change. The polypyrrole is more difficult to drive to as low a conductivity as found for the poly-3-methylthiophene. Since the geometry of the microelectrode/polymer assemblies is not well-defined, it is somewhat difficult to assess the conductivity of the oxidized polymer. However, we estimate the conductivity of the poly-3-methylthiophene to be $10^2 \Omega^{-1} \text{ cm}^{-1}$, in rough accord with literature reports¹ of the conductivity of this polymer measured by other methods. There is an obvious correlation of the potential dependence of optical (Figure 1), charging (Figure 2), and resistance (Figure 5) properties of poly-3-methylthiophene.

Characteristics of poly-3-methylthiophene-Based Microelectrochemical

Transistors. Removal of a small amount of electrical charge from the poly-3-methylthiophene coating two microelectrodes increases the conductivity

"channel" region beneath the gate oxide.¹⁶ Two important differences limit the utility of the microelectrochemical device in traditional applications of transistors. The first difference is that the channel thickness of a state-of-the-art MOSFET is much smaller than the thickness of the polymer. This results in the need for a relatively large amount of charge to turn on the microelectrochemical devices. We typically work with poly-3-methylthiophene-based devices where a fraction of 10^{-7} moles of e^-/cm^2 must be withdrawn from the polymer to turn on the device. In absolute terms $\sim 10^{-13}$ moles of e^- 's must be withdrawn to substantially turn on the devices. A Si MOSFET can be turned on with $\sim 10^{-12}$ moles of e^-/cm^2 of gate area. Thus, while the turn on/turn off V_G changes for a microelectrochemical transistor and a solid state device are similar, the charge required in the microelectrochemical device is significantly larger. This means that the amplification of power will be less with the microelectrochemical device. The point is that the gate current for the microelectrochemical devices is substantially larger than for a solid state amplifier.

In principle, the minimum amount of the polymer necessary to connect two microelectrodes can be lowered considerably, and work toward this aim is underway in this laboratory. The second difference of consequence in using a redox polymer, albeit a conducting polymer, as the "channel" material is that the charge needed to turn on the device is associated with the movement of ionic species into polymer. The electrochemical conversion of poly-3-methylthiophene from insulating to conducting involves chemical changes, whereas the changes in current flow between source and drain in a solid state FET are a consequence of the movement of capacitive charge and there is no ion movement. Though the conducting polymer can, in principle, be much thinner than employed here ion movement is still required and the turn on/

turn off rate will be slower than for solid state devices. The point is that the frequency of operation of the microelectrochemical device is limited by oxidation/reduction times. Redox polymers (at thicknesses of several tenths of a micron) have been electrochemically driven between oxidized and reduced states at frequencies of the order of 10 Hz.¹⁷ Figure 7 shows data demonstrating that the poly-3-methylthiophene-based microelectrochemical transistor can be turned on and off rapidly on the one second timescale. By monitoring the turn on and turn off using an oscilloscope we find that the device can be turned on (V_G stepped from 0.0 V to +0.9 V vs. SCE) within 20-50 ms and turned off (V_G stepped from +0.9 V to 0.0 V vs. SCE) within 20 ms. These are the best characteristics of any molecule-based transistor reported so far.²⁻⁴

Applying a sinusoidal change of V_G , negative limit = 0.0 V and positive limit = +0.9 V vs. SCE, at 10 Hz shows that substantial power gain can be realized with a poly-3-methylthiophene-based transistor. Under such conditions the maximum gate current is $\sim 1 \mu A$ while the maximum I_D at $V_D = 0.2$ V is ~ 1 mA. Substantial loss in power amplification occurs between 10 and 100 Hz under these conditions. When the device is driven with a sinusoidal V_G between +0.4 V and +0.9 V vs. SCE the response can be better, because the device is partially "on" at +0.4 V. A detailed study of the power amplification properties will be reported elsewhere, but for now it is worth noting that power amplification of about 1000 can be obtained at 10 Hz with the power in the gate circuit associated with the charge passed in the potential sweep between 0.0 V (fully off) and +0.9 V vs. SCE (fully on).

Response of Poly-3-methylthiophene-Based Microelectrochemical Device to a Repetitive, Reproducible Chemical Signal. An interesting finding is that the poly-3-methylthiophene-based microelectrochemical transistor is durable in

aqueous electrolyte over a wide pH (1 to 9) range. Figure 8 shows a typical test of durability at pH \approx 7. At a V_D of 0.1 V and $V_G = +0.5$ V vs. SCE a nearly constant (and large) I_D is found for a period of 6 h. During the 6 h $\sim 15C$ of charge pass through each electrode/polymer interface, corresponding to $\sim 15 \times 10^6$ C/cm². A cyclic voltammogram before and after the durability test shows some loss of material, but the device characteristics (I_D vs. V_D at fixed V_G and I_D vs. V_G at fixed V_D) were essentially unchanged. The fact that loss of polymer material does not affect the device performance suggests that excess polymer was present initially, and the electrodes remain effectively connected with polymer even though some loss occurs with time. Experiments to demonstrate ~ 10 Hz operation (Figure 6 and vide supra) of the microelectrochemical transistor also establishes substantial durability, since in such experiments the devices have been demonstrated to undergo thousands of on-off cycles with no change in device performance.

The electrochemical characterization of the poly-3-methylthiophene-based device, Scheme Ia, shows that useful microsensors could be made if the chemical signal could equilibrate with the polymer to oxidize or reduce it to turn on or off, respectively, the device, Scheme Ib. To demonstrate the performance of the poly-3-methylthiophene-based device in such a situation we have placed the device in the effluent stream of an HPLC and made repetitive injections of a chemical oxidant into the system. Figure 9 shows the response to six injections of K_2IrCl_6 in aqueous electrolyte. The experiment was continued for 30 h and the reproducibility was invariant. In the experiment summarized by Figure 9 the device is "turned on" by the oxidant $IrCl_6^{2-}$, E°' ($IrCl_6^{2-}/3^-$) = +0.68 V vs. SCE,¹⁸ but it is not clear what it is that turns off the device. Oxidation of the poly-3-methylthiophene by the $IrCl_6^{2-}$ should not, in principle, be reversed by the flowing H_2O /electrolyte.

However, the background impurity level of some reducing agent(s) is clearly sufficient to switch the device off. Accordingly, the time to switch off the device depends on the solvent/electrolyte purity. In some experiments the device could only be switched off by the purposeful injection of a reductant, e.g. $\text{Fe}(\text{CN})_6^{4-}$, to reduce the oxidized poly-3-methylthiophene. In such cases repetitive alternate injection of IrCl_6^{2-} and $\text{Fe}(\text{CN})_6^{4-}$ demonstrates rapid turn on/turn off cycles with no loss in reproducibility over many injections.

The ability to reproducibly activate a device like that in Scheme Ib with chemical redox reagents is demonstrated by the experiments described above. Further details establish that "amplification" of the chemical signal is possible. In the IrCl_6^{2-} experiment, the number of oxidizing equivalents injected is 4×10^{-7} moles and the integral of the I_D vs. time plot for each injection shows that only 7.5×10^{-9} moles of electrons pass. However, the amount of IrCl_6^{2-} that actually reaches the surface of the polymer is only a small fraction of the total IrCl_6^{2-} injected, owing to the geometry used in the experiments. The eight-electrode array used for the experiment in Figure 9 is one like that depicted in Figure 3 with several of the electrodes as "naked" electrodes. A pair of the naked electrodes can be used to determine the amount of IrCl_6^{2-} that is available at the surface of the polymer-based transistor. A pair of electrodes is used to simulate the area of the transistor. The measurement involves injecting the IrCl_6^{2-} (4×10^{-7} moles) and measuring the current corresponding to the reduction of IrCl_6^{2-} to IrCl_6^{3-} at the naked electrodes held at 0.0 V vs. SCE. The integral of the reduction current vs. time plot (3.2×10^{-8} C) shows that $3.2 \times 10^{-13} \pm 20\%$ moles of IrCl_6^{2-} are reduced on each injection. This means that only about $8 \times 10^{-5} \%$ of the injected IrCl_6^{2-} actually reaches the transistor. Thus, the amplification of the chemical signal can be regarded to exceed 2×10^4 using

the poly-3-methylthiophene-based device. Further work is needed to improve the effluent/device geometry, but the essential result is clear: the poly-3-methylthiophene-based device responds reproducibly to amplify chemical signals.

Increase in I_D of the poly-3-methylthiophene sensor occurs in response to $\sim 1 \times 10^{-9}$ mole of IrCl_6^{2-} injected. Assuming that the fraction coming to the surface of the transistor is $8 \times 10^{-5}\%$, this means that the device responds to 8×10^{-16} moles of the oxidant. With such an injection reduction of the IrCl_6^{2-} to IrCl_6^{3-} at the two naked electrodes could not be detected with the equipment available. The point is that while the deposited poly-3-methylthiophene is typically used in an amount that requires $\sim 10^{-12}$ moles of oxidizing equivalents to turn it completely on, some small fraction ($< 10^{-3}$) can give an easily measured change in I_D . Effort in this laboratory is now directed towards functionalizing the poly-3-methylthiophene to bring about response to specific oxidants and reductants.

Acknowledgements. We thank the Defense Advanced Research Projects Agency and the Office of Naval Research for partial support of this research.

References

1. (a) R.J. Waltman, J. Bargon, A.F. Diaz, J. Phys. Chem., 1983, 87, 1459;
(b) G. Tourillon, F. Garnier, J. Phys. Chem., 1983, 87, 2289; (c) G. Tourillon, F. Garnier, J. Electroanal. Chem., 1983, 148, 299; (d) S. Hotta, T. Hosaka, W. Shimotsuma, Synth. Met., 1983, 6, 317; (e) H. Neugebauer, G. Nauer, A. Neckel, G. Tourillon, F. Garnier, P. Lang, J. Phys. Chem., 1984, 88, 652; (f) G. Horowitz, G. Tourillon, F. Garnier, J. Electrochem. Soc., 1984, 131, 151; (g) G. Tourillon, F. Garnier, D. Gourier, D. Vivien, J. Phys. Chem., 1984, 88, 1049; (h) S. Glenis, G. Horowitz, G. Tourillon, F. Garnier, Thin Solid Films, 1984, 111, 93; (i) G. Tourillon, F. Garnier, J. Electroanal. Chem., 1984, 161, 407; (j) G. Tourillon, F. Garnier, J. Electroanal. Chem., 1984, 161, 51; (k) R. J. Waltman, A.F. Diaz, J. Bargon, J. Electrochem. Soc., 1984, 131, 740; (l) S. Hotta, T. Hosaka, M. Soga, W. Shimotsuma, Synth. Met., 1984, 9, 87.
2. H.S. White, G.P. Kittlesen, M.S. Wrighton, J. Am. Chem. Soc., 1984, 106, 5375.
3. G. P. Kittlesen, H.S. White, M.S. Wrighton, J. Am. Chem. Soc., 1984, 106, 7389.
4. E.W. Paul, A.J. Ricco, M.S. Wrighton, J. Phys. Chem., 1985, 81, 1441.
5. (a) G.P. Kittlesen, H.S. White, M.S. Wrighton, submitted for publication to J. Am. Chem. Soc.; (b) G.P. Kittlesen, M.S. Wrighton, submitted for publication to J. Mol. Electron.
6. W. Fichtner, E.N. Fuls, R.L. Johnston, R.K. Watts, W.W. Weick, I.E.D.M. 1983 Technical Digest, 1983, 383.
7. G. P. Kittlesen, Ph.D. Thesis, M.I.T. 1985.
8. T.-C. Chung, J.H. Kaufman, A.J. Heeger, F. Wudl, Phys. Rev. B., 1984, 30, 302.

9. A.F. Diaz, J.I. Castillo, J.A. Cogan, W.-Y. Lee, J. Electroanal. Chem., 1981, 129, 115.
10. R.A. Bull, F.-R. Fan, A.J. Bard, J. Electrochem. Soc., 1982, 129, 1009.
11. P.J. Pearce, A.J. Bard, J. Electroanal. Chem., 1980, 114, 89; 1980, 112, 97; 1980, 108, 121; (b) P. Daum, R.W. Murray, J. Phys. Chem., 1981, 85, 389-396; (c) P. Daum, J.R. Lenhard, D. Rolison, R.W. Murray, J. Am. Chem. Soc., 1980, 102, 4649-4653.
12. T.J. Lewis, H.S. White, M.S. Wrighton, J. Am. Chem. Soc., 1984, 106, 6947.
13. See the discussion of the electrochemical conversion of polypyrrole to its conducting state: S.W. Feldberg, J. Am. Chem. Soc., 1984, 106, 4671.
14. B.J. Feldman, P. Burgmayer, R.W. Murray, J. Am. Chem. Soc., 1985, 107, 872.
15. (a) R. L. Greene, G.B. Street, Science, 1984, 226, 651; (b) R.W. Munn, Chemistry in Britain, 1984, 518; (c) C.B. Duke, H.W. Gibson, "Conductive Polymers," in Kirk-Othmer Encyclopedia of Chemical Technology, 18, 744; Wiley: New York, 1982; (d) G. Wegner, Angew. Chem. Int. Ed. Engl., 1982, 20, 361; (e) J. E. Frommer, R.R. Chance, "Conducting Polymers" in Encyclopedia of Polymer Science and Engineering, M. Grayson, J. Kroschwitz, eds., Wiley: New York [In Press].
16. S.M. Sze, "Physics of Semiconductor Devices"; Wiley: New York, 1981.
17. (a) D.C. Bookbinder, M.S. Wrighton, J. Electrochem. Soc., 1983, 130, 1080; (b) R. W. Murray, "Electroanalytical Chemistry: vol. 13", A.J. Bard ed.; Marcel Dekker: New York, 1984.
18. J. A. Bruce, M.S. Wrighton, J. Am. Chem. Soc., 1982, 104, 74.

Figure Captions

Figure 1. Optical spectral changes accompanying the change of potential of a partially optically transparent Au electrode coated with a film of poly-3-methylthiophene. The data are for $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ electrolyte solution.

Figure 2. Charge passed (mC/cm^2) following a potential step of Pt electrodes from a given potential to 0.0 V vs. SCE as a function of the thickness of film of poly-3-methylthiophene anodically grown onto the Pt electrode. The inset shows the capacitance per cm^2 vs. thickness of the polymer. The capacitances are from the straight line portion of the mC/cm^2 vs. potential plots, i.e. positive of +0.5 V vs. SCE.

Figure 3. Scanning electron micrographs of naked microelectrode array (top) and a poly-3-methylthiophene derivatized array (bottom). The derivatized array at the bottom was functionalized by oxidizing 3-methylthiophene at the three microelectrodes on the right while holding the five microelectrodes on the left at a potential of -1.0 V vs. SCE.

Figure 4. Cyclic voltammetry ($\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$) response of two adjacent and connected poly-3-methylthiophene-coated microelectrodes as a function of sweep rate. The crucial result is that the area under each current-potential scan (at a given linear sweep rate) is the same for wire A, wire B, and wires A + B driven as one electrode. These results show that for the sweep rates shown that all of the polymer accessible to A is equally accessible to B, allowing the conclusion that the microelectrodes A and B are connected with poly-3-methylthiophene.

Figure 5. Current-potential curves ($\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$) as a function of the gate potential (top) for a pair of poly-3-methylthiophene connected microelectrodes. The potential of one of the microelectrodes is varied a small amount ($\sim \pm 20 \text{ mV}$) around the gate potential. The bottom portion of the figure shows the resistance between the two microelectrodes as a function of gate potential.

Figure 6. Transistor characteristics, I_D , vs. V_D at fixed V_G (left) and I_D vs. V_G at fixed V_D (right), for a poly-3-methylthiophene-coated microelectrode array. I_D vs. V_G data are steady state data and the I_D vs. V_G curves are at 5 mV/s .

Figure 7. Turn on/turn off characteristics of a poly-3-methylthiophene-based transistor in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$. The turn on is effected by a step of V_G from 0.0 to $+0.9 \text{ V}$ vs. SCE and turn off is effected by step of V_G from $+0.9 \text{ V}$ to 0.0 V vs. SCE at $V_D = 0.1 \text{ V}$. The experiment was carried out for ~ 4 hours without change in the turn on/turn off characteristics. The risetime and falltime is $< 50 \text{ ms}$ as recorded with an oscilloscope. The value of I_D in the on state is $> 95\%$ of the steady state value.

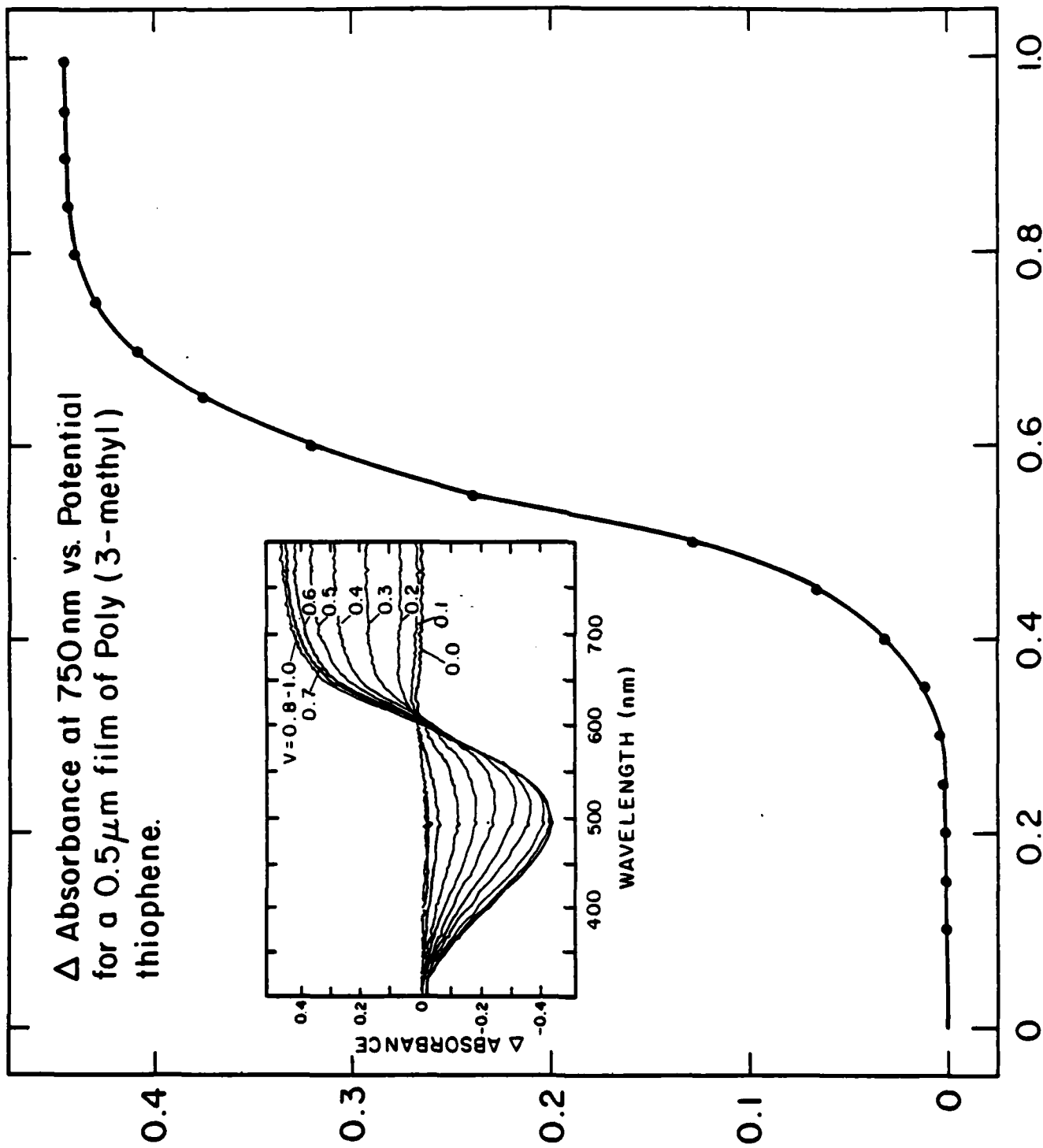
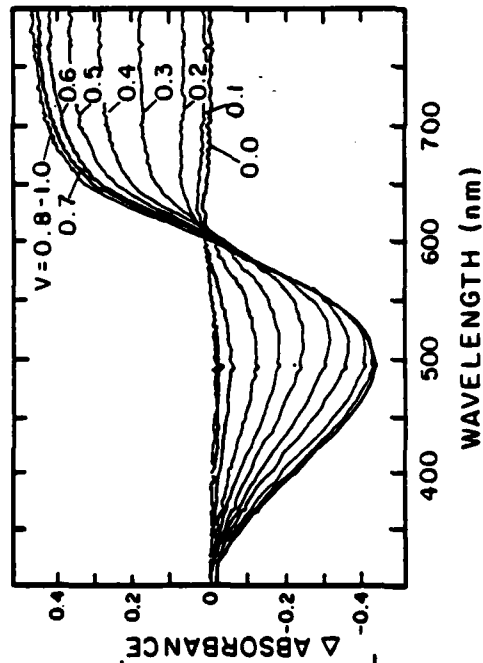
Figure 8. Cyclic voltammetry ($\text{H}_2\text{O}/1.0 \text{ M } \text{LiClO}_4$) (inset) of poly-3-methylthiophene on connected microelectrodes before and after stability test of 6 h . The stability test consisted of holding the transistor in the on state, $V_G = 0.5 \text{ V}$ vs. SCE at a $V_D = 0.1 \text{ V}$ in an aqueous $1.0 \text{ M } \text{LiClO}_4$ solution. The principal plot shows I_D vs. time for the transistor.

Figure 9. Change in I_D with time of a poly-3-methylthiophene-based transistor placed in the effluent stream ($0.1 \text{ M NaClO}_4/0.05 \text{ M NaH}_2\text{PO}_4$) of high pressure liquid chromatograph. An aqueous solution of K_2IrCl_6 was injected automatically every eight minutes into the electrolyte solution to provide a repetitive exposure to an oxidant, IrCl_6^{2-} , capable of turning on the transistor. Background (reductant) impurity in the solvent/electrolyte turns the device off. The value of $V_D = 0.1 \text{ V}$, and the device is simply exposed to the flowing effluent stream as represented in Scheme Ib.

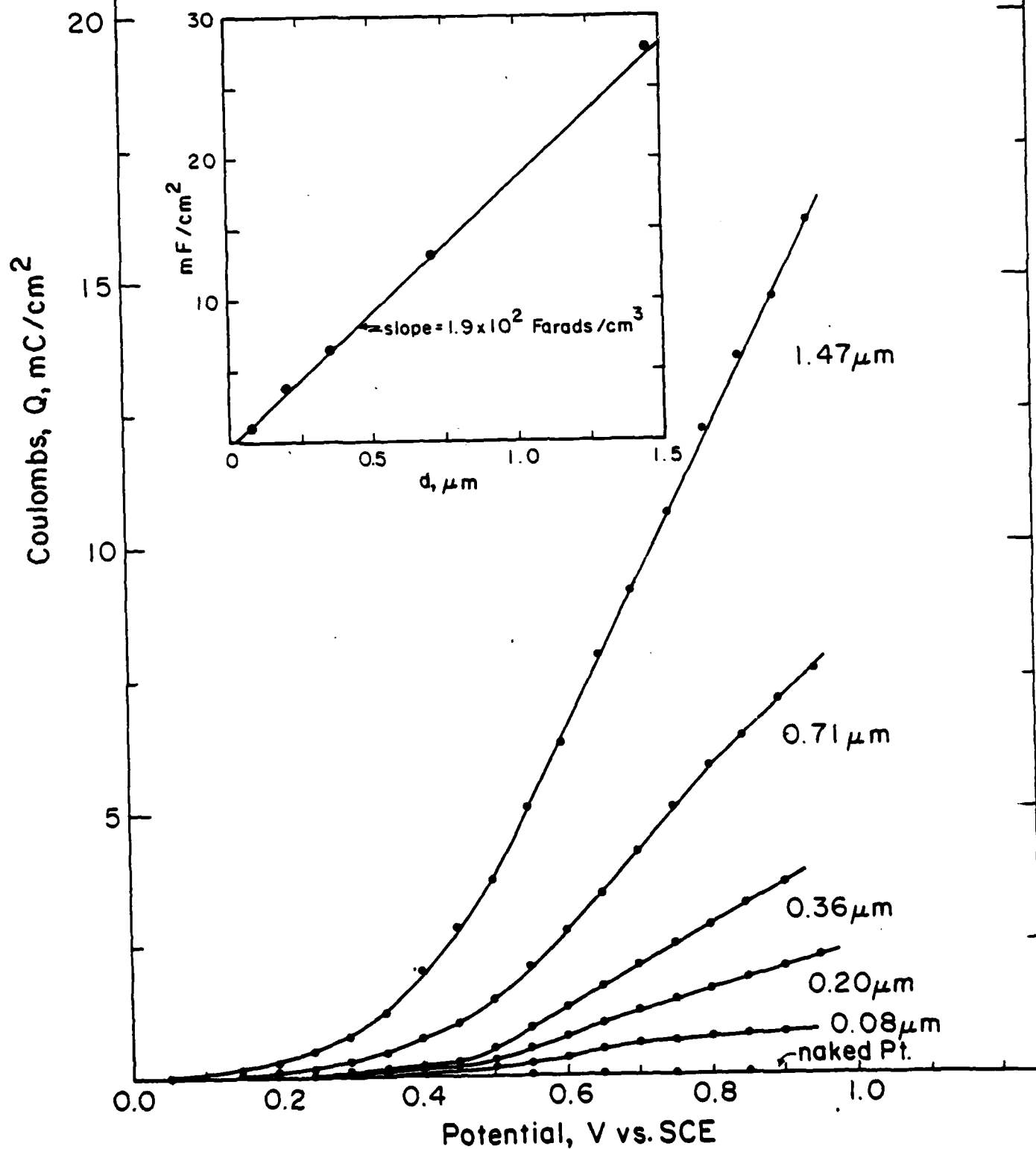
Δ Absorbance at 750nm vs. Potential
for a 0.5 μ m film of Poly (3-methyl)
thiophene.

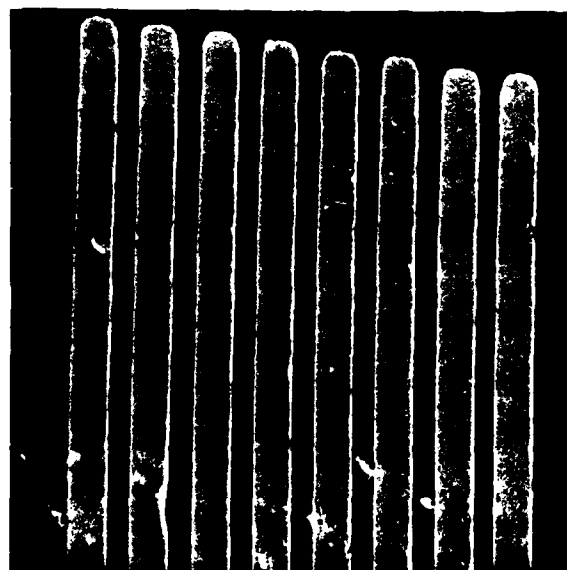
Δ Absorbance at 750 nm

Potential, V vs. SCE



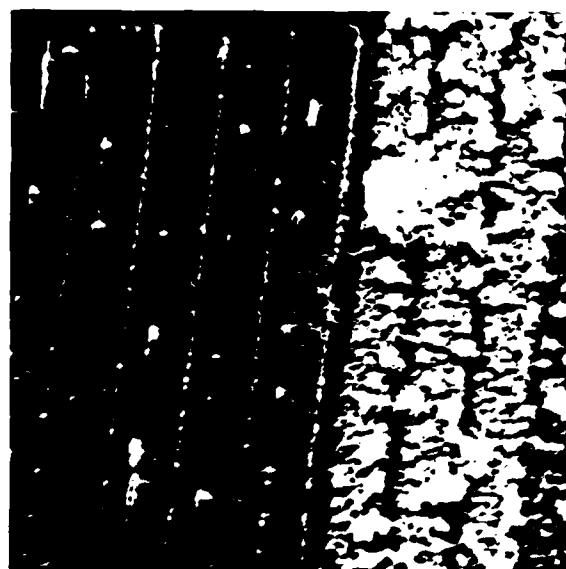
Potential-Step Chronocoulometry for
Poly(3-methyl) thiophene on Pt.
 $\text{CH}_3\text{CN}/0.1\text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$





5.0 μ

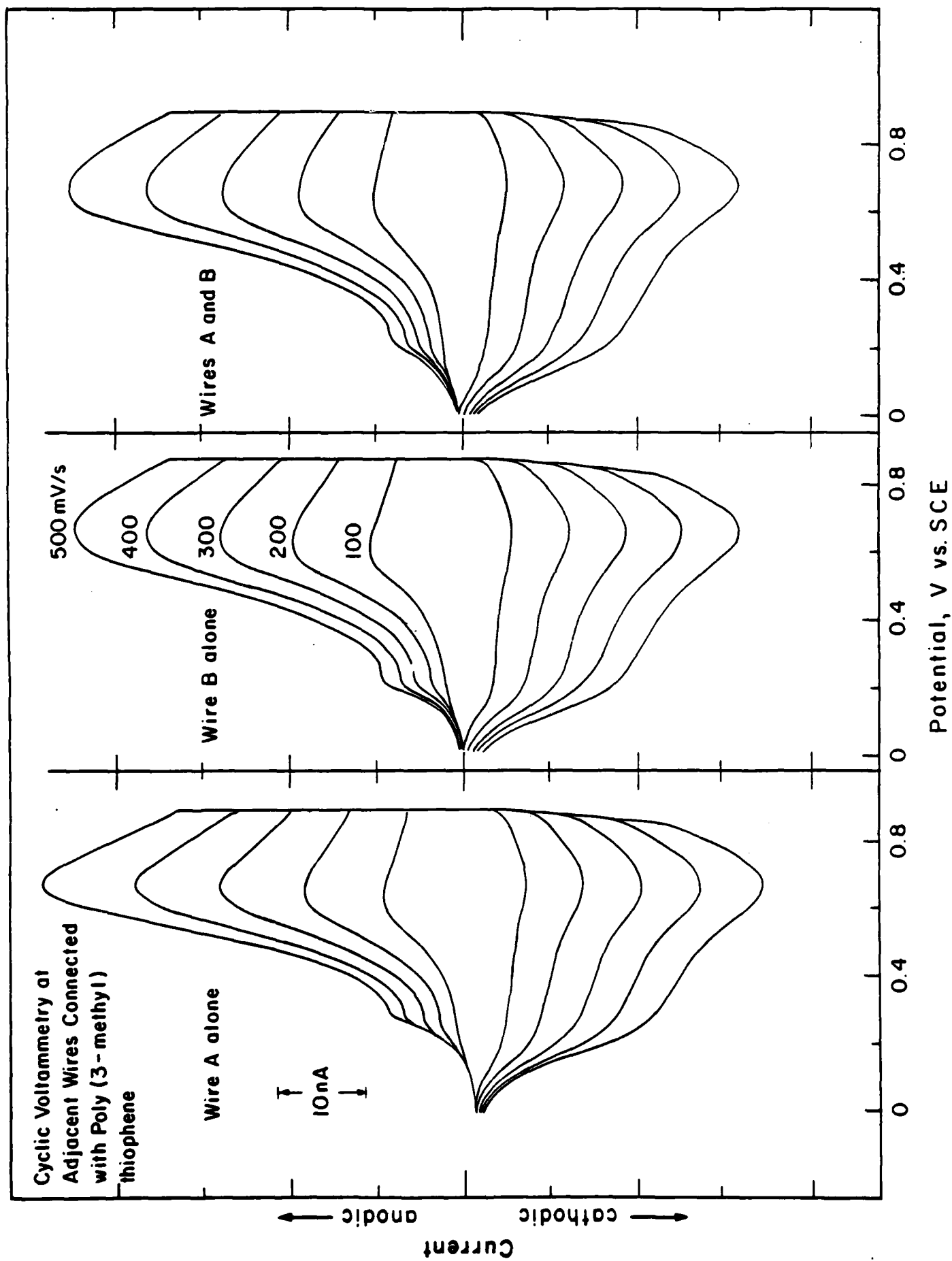
Microelectrode array
prior to derivatization

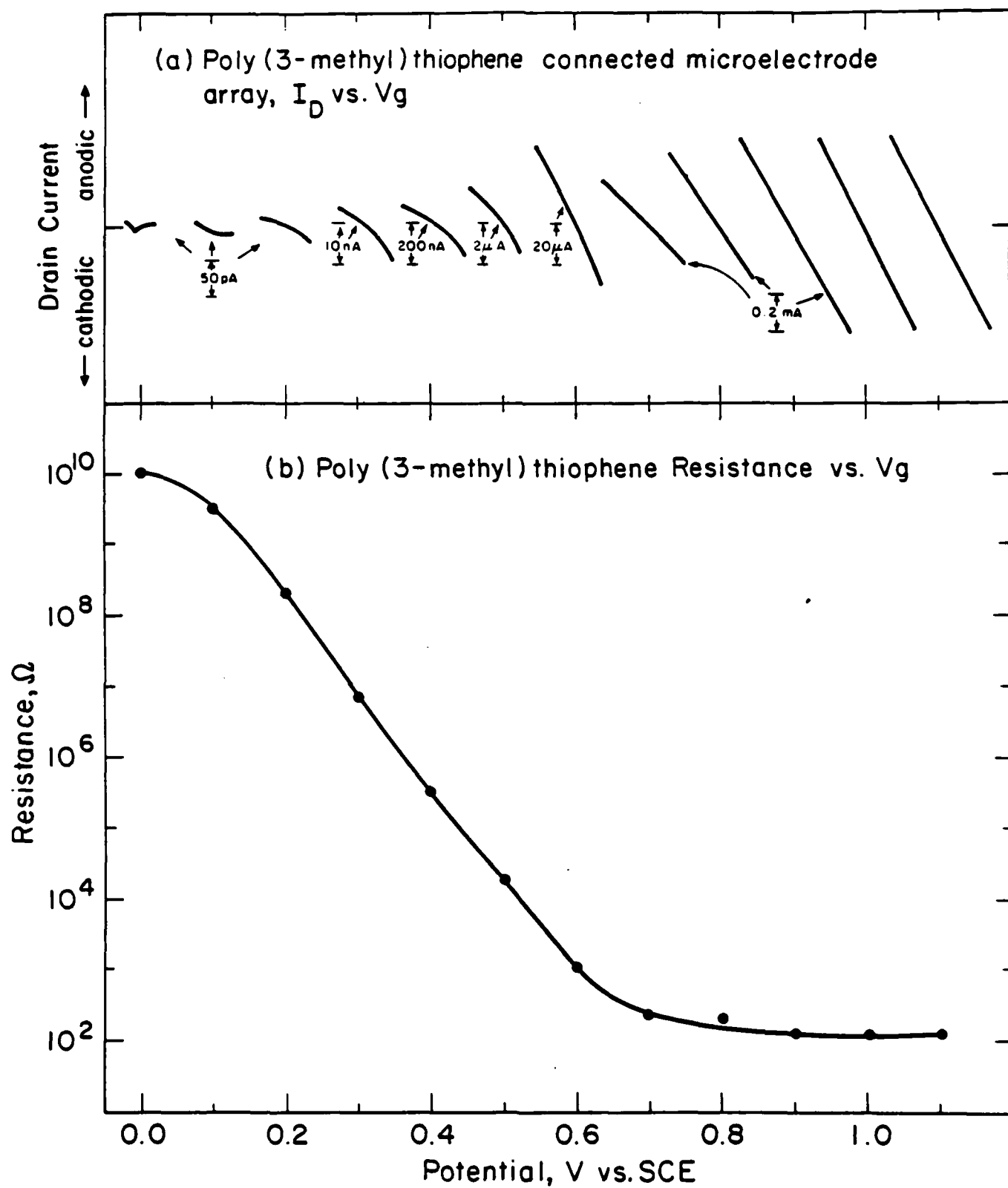


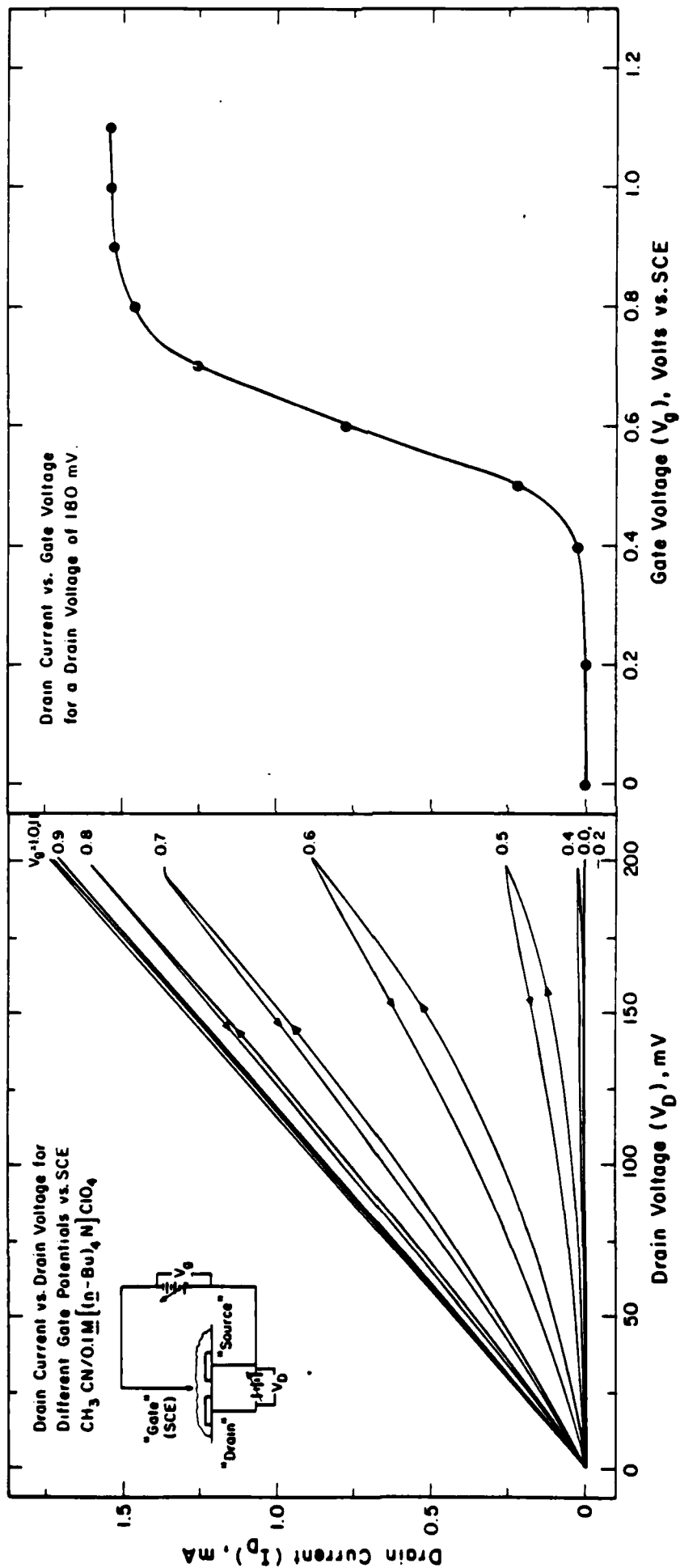
5.0 μ

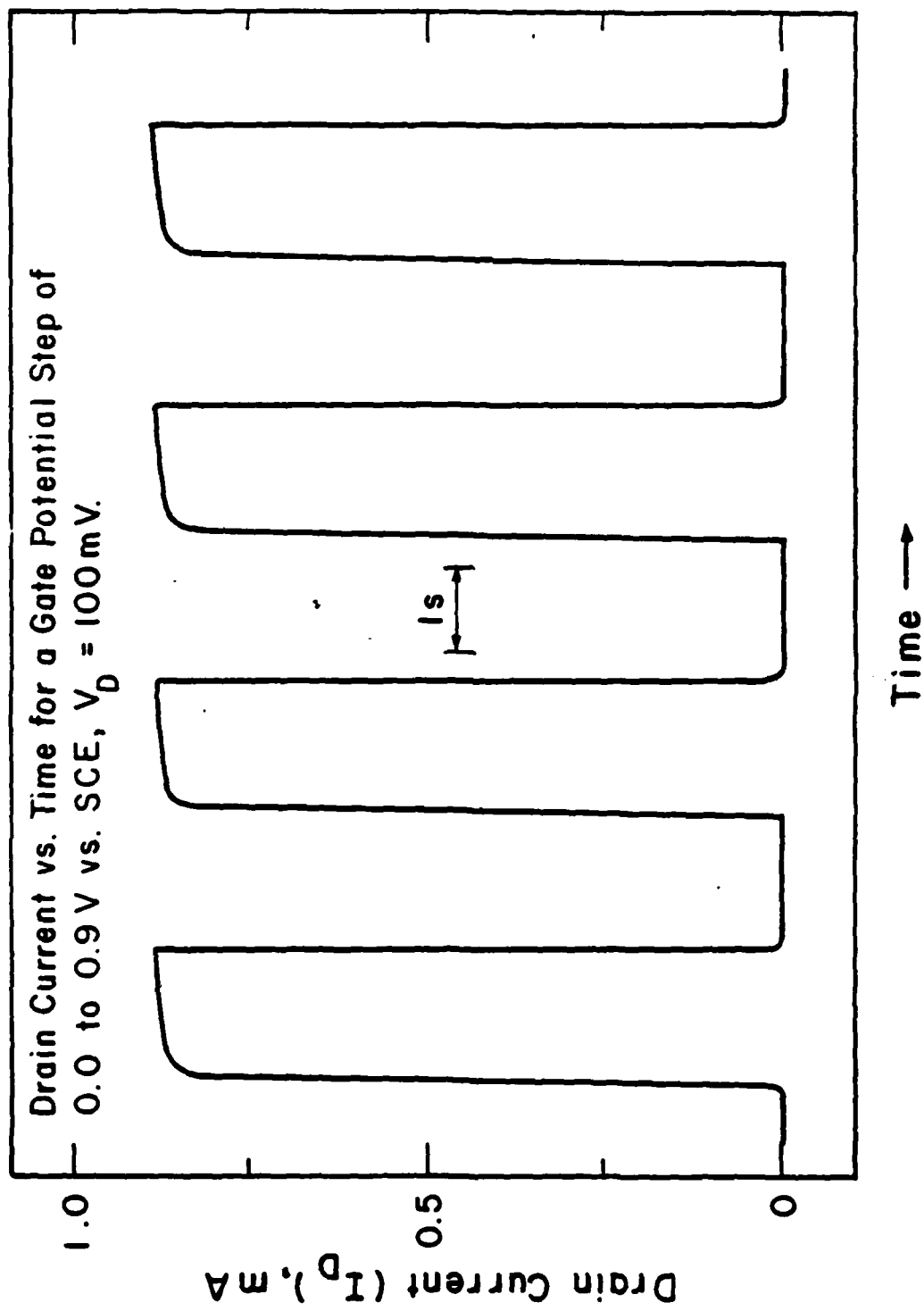
Microelectrode array
derivatized with Poly-
(3-methyl) thiophene.

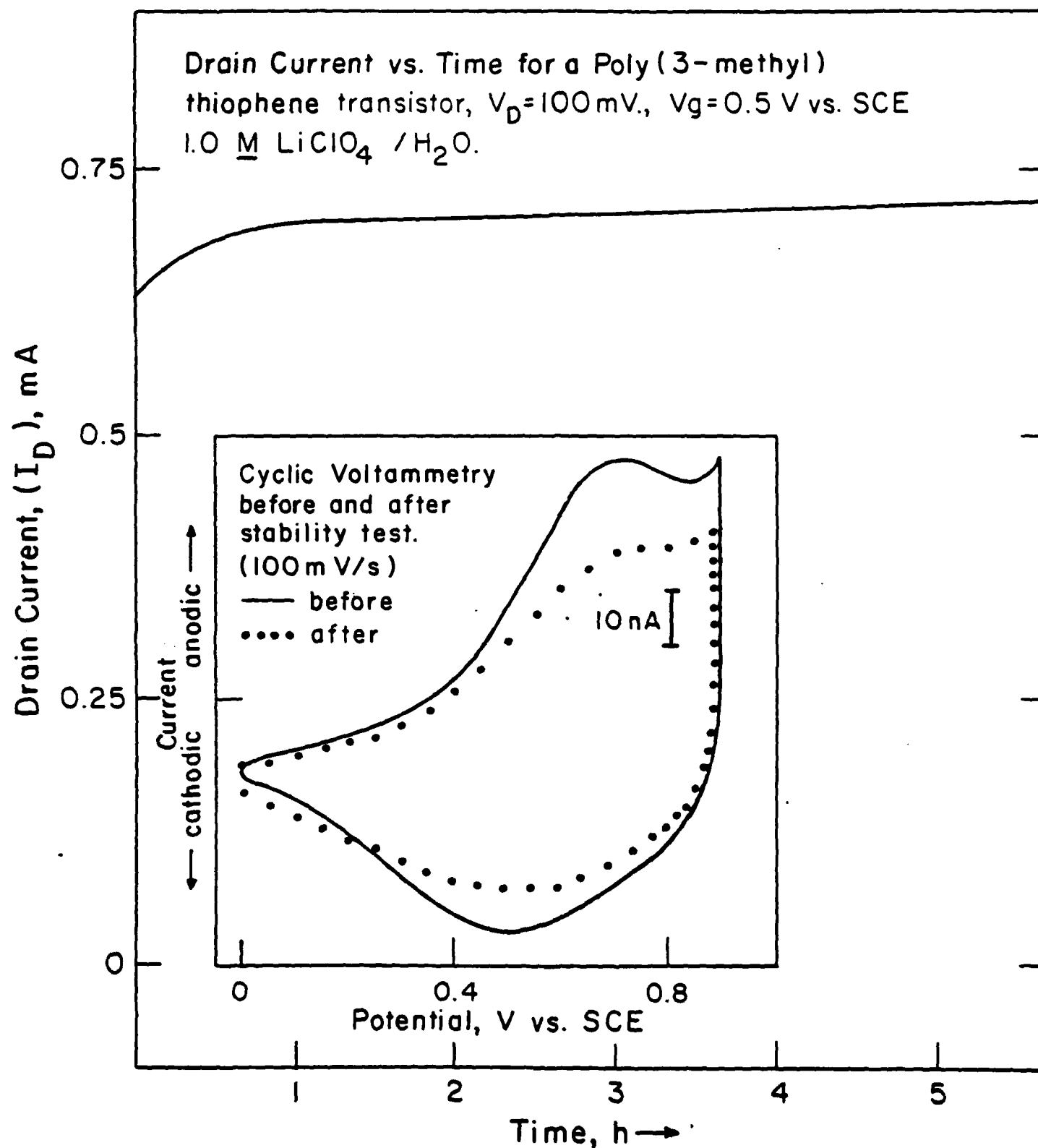
Three electrodes on right
shown to be connected
through conducting polymer
and constitute a
microelectronic device.





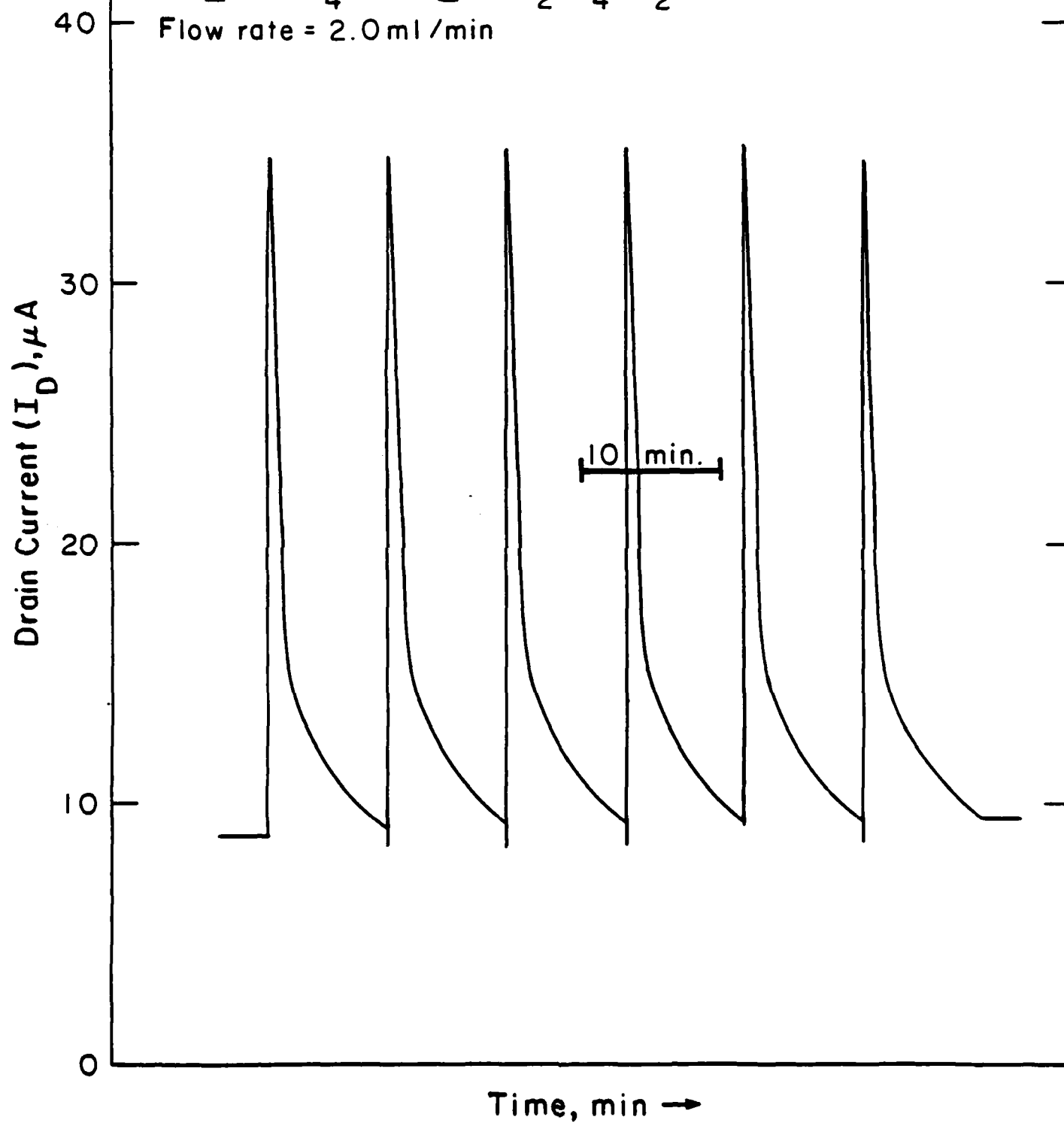






Chemical Stimulus of Poly(3-methyl) thiophene
transistor through 0.4 μ mole injections of K_2IrCl_6
0.1M $NaClO_4$ / 0.05M NaH_2PO_4 / H_2O .

Flow rate = 2.0 ml / min



DISTRIBUTION LIST

All Reports

Molecular Biology Program, Code 441MB
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

Annual, Final and Technical Reports

Defense Technical Information Center (2 copies)
Building 5, Cameron Station
Alexandria, VA 22314

Annual and Final Reports Only (one copy each)

Scientific Library
Naval Biosciences Laboratory
Naval Supply Center
Oakland, CA 94625

Commanding Officer
Naval Medical Research & Development Command
National Naval Medical Center
Bethesda, MD 20814

Director
Infectious Disease Program Center
Naval Medical Research Institute
National Naval Medical Center
Bethesda, MD 20814

Commander
Chemical and Biological Sciences Division
Army Research Office
Research Triangle Park, NC 27709

Commander
U.S. Army Research and Development Command
Attn: SGRD-PLA
Fort Detrick
Frederick, MD 21701

Commander
USAMRIID
Fort Detrick
Frederick, MD 21701

Commander
Air Force Office of Scientific Research
Bolling Air Force Base
Washington, DC 20332

Administrative Contracting Officer
Office of Naval Research Laboratory
(address varies - obtain from Business Office)

Final and Technical Reports Only

Director, Naval Research Laboratory (6 copies)
Attn: Code 2627
Washington, DC 20375

END

FILMED

10-85

DTIC