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For the Degree of Master of Science

TITLE   PHOTOELECTROCHEMISTRY WITH POLYMER SEMICONDUCTORS:

POLY(CHROME AZUROL S-ACETYLENE)

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ACCEPTED BY THE DEPARTMENT OF Chemistry

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ABSTRACT

PHOTOELECTROCHEMISTRY WITH POLYMER SEMICONDUCTORS:
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Alan J. Oleksa

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The present work is concerned with producing a polymer semiconductor which could photocatalyze the decomposition of water. The method chosen to couple an acetylene, (conductive polymer), to an organic dye, (light absorber), was the Williamson ether synthesis. If polymerized, the intention was that the polymer would be conductive, while the organic dye would branch off the polymer as a "pendent" group and be a necessary ingredient for an electrical gradient, separating a charge and producing a chemical potential, when light illuminated the polymer.

The structure of the "dye derivatized" acetylene was confirmed with the use of nmr, ir, and TLC data. Cyclic voltammetry was employed as a tool in determining any electroactive species in the dye. The cyclic voltammograms confirmed the presence of a conductive layer on the surface of the electrode, consistent with that of electropolymerizations, but was unstable upon exposure to air, and wouldn't conduct when reimmersed in electrolyte solution.

ACKNOWLEDGEMENTS

I would like to thank Dr. Howard D. Mettee whose guidance and understanding made this thesis possible.

I would also like to extend my appreciation to Dr. Daryl Mincey and Dr. Stephen Schildcrout for their time and effort reviewing the manuscripts.

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LIST OF SYMBOLS

SYMBOL	DEFINITION	UNITS
C_b	Conduction band	
V_b	Valence band	
e^-	electron	
h^+	hole	
E_f	Fermi level	eV
E_{fb}	Flat band potential	eV
E_f^o	Standard potential of redox couple	eV
μA	Microamperes	10^{-6} amps
Ox	Oxidized species of redox couple	
Red	Reduced species of redox couple	
$S^{\cdot}$	Neutral soliton	
S^+	Positively charged soliton	
S^-	Negatively charged soliton	
ρ	Resistivity	ohm·cm
σ	Conductivity	$(ohm \cdot cm)^{-1}$
E_g	Band gap potential	eV
$(CH)_x$	Polyacetylene; also poly(CH)	
PEC	Photoelectrochemical	
CV	Cyclic voltammetry	
v	Scan rate	mV/sec

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CHAPTER I

INTRODUCTION

General

Conducting polymers have opened a new field in photoelectrochemistry whose potential has yet to be exploited. One use of conducting polymers is to employ solar energy to split water into oxygen and hydrogen, where hydrogen could be a useful source of energy on earth. One conductive polymer of interest in this thesis is polyacetylene, $(CH)_x$, whose properties may aid in photoelectrochemistry. As Mettee[1] states, polymers may play a central role in light absorption, charge separation, and particle flow dynamics that make up part of the photoelectrochemical (PEC) process.

> "The solar energy coming down onto the earth's surface amounts to ca. 3×10^{24} J per year, which is about 10^4 times the world-wide yearly energy consumption."[2]

Why not harness some of the sun's radiant energy? For systems converting solar energy into electrical, Watanabe[3] has elaborated on two criteria. First, there has to be absorption by a "chemical substance" of solar energy which would be able to cause the separation of electron (e^-)-hole (h^+) pairs. The second factor to consider is to separate these e^-/h^+ pairs with minimum loss due to recombination.

In order that this charge separation proceeds effectively, there should be a potential gradient established where this excitation takes place. It was pointed out that a way to create a potential gradient is by "band bending" in a semi-conductor material at the interface of a liquid junction. When a semiconductor is used as an electrode, and it is connected to a counter electrode, photoexcitation of the semi-conductor can generate a chemical potential to cause a redox reaction on the surface of the electrode. Another example of such an interface is the lipid membrane of the chloro-plast of green plants, which is a very economic and dur-able form of solar converter.

Band Theory of Semiconductors

Energy bands originate in semiconductors when atoms are brought into a collection to form a solid. The Pauli Exclusion Principle has to be obeyed, and so discrete atomic levels are formed into bands of levels in the solid, (Fig-ure 1). At absolute zero temperature, lower energy levels are filled first before higher levels so that the upper levels are empty. The highest filled level is known as the valence band (V_b). The Fermi energy (E_f) is characteristic of the chemical potential of electrons in a semiconductor. Holes also have a Fermi level.

Insulators, metals, and semiconcuctors can be com-pared by the width of band gap between valence and conduc-tion bands (C_b), corresponding to the Homo and Lumo levels

in molecules as shown in Figure 2. An insulator usually results
when the band gap is several eV or more. The energy which
is required to excite an electron to the next band is the
band gap energy. At room temperature, there isn't enough
thermal energy for excitation to occur and the solid is an
insulator. Conversely, a metal contains no band gap, since
its upper levels in the band are only partially filled.
Electrons can move between the partially filled levels
in the same band easily. An intrinsic semiconductor shows
that the valence band is full while the conduction band is
empty at absolute zero. At 0 K semiconductors are insulators,
but as temperature rises, and thermal energy increases,
electrons are excited from the valence band into the conduc-

Fig. 1. Energy levels for electrons in the
outer shells of a free atom (Right). Energy bands
for the electrons in a solid are shown also (Left).
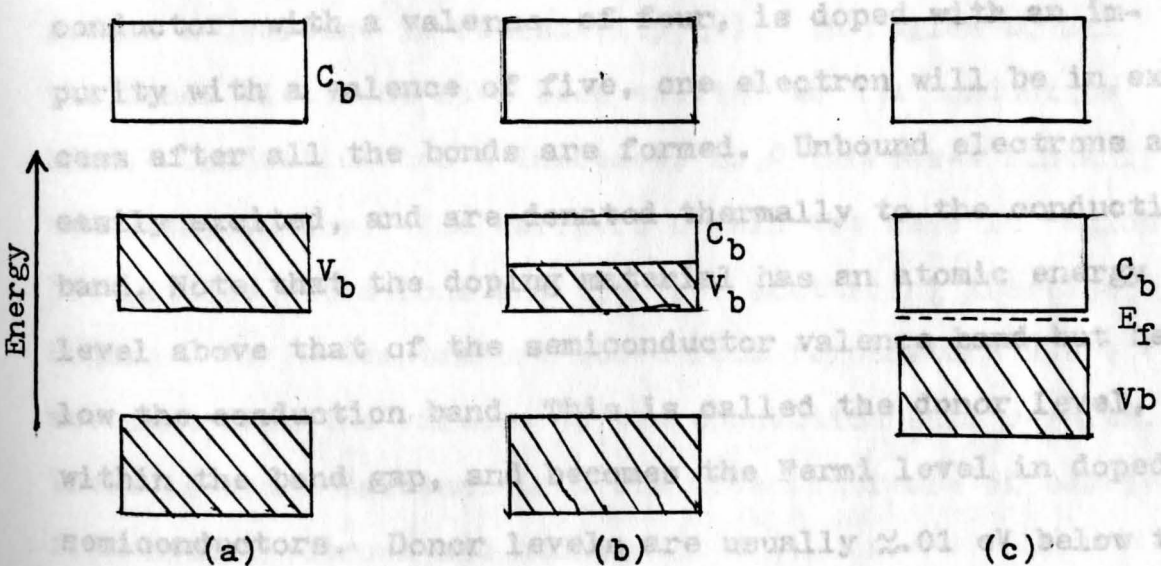
Fig. 2. Energy bands for an insulator, (a), a
metal (b), and an intrinsic semiconductor (c).

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but as temperature rises, and thermal energy increases,
electrons are excited from the valence band into the conduc-
tion band leaving holes in the valence band. (Figure 3)

When an element such as silicon, an intrinsic semi-
conductor with a valence of four, is doped with an im-
purity with a valence of five, one electron will be in ex-
cess after all the bonds are formed. Unbound electrons are
easily excited, and are donated thermally to the conduction
band. Note that the doping material has an atomic energy
level above that of the semiconductor valence band but be-
low the conduction band. This is called the donor level,
within the band gap, and becomes the Fermi level in doped
semiconductors. Donor levels are usually $\approx.01$ eV below the C_b.

If silicon is doped with an impurity atom with a
valence of three, there will be an absence of a bonding
electron after all the bonds are formed between the atoms.

In this case, the atomic level of the dopant has a Fermi
level within the band gap close to the valence band, where
electrons can jump easily. This becomes the acceptor state
of the semiconductor, $\approx$ .01 eV from the valence band (Fig. 4).

The difference between these doped semiconductors
lies in the majority carriers. The donor impurity results in
the conduction of electrons in the conduction band, and con-
versely, when acceptor levels accept electrons from the valence
band, there is conduction by holes (h^+) in the conduction
band. These are known as n-type and p-type semiconductors,
respectively.

A plot of resistivity versus temperature (Figure 5)
of an n-type semiconductor, as it is brought from 0 K, shows
that region A, about 10 K, has enough energy to empty the
donor state electrons into the conduction band. This is
seen as a decrease in resistivity (ρ). In region B, all
the donor electrons have been excited to the conduction
band. Conduction can't increase, so ρ increases linearly
with temperature. The carriers remain the same in region B,
but lattice vibrations and electron scattering increase ρ.
Region C is a temperature above room temperature where e^-
movement from the valence to the conduction band results.
There is now a decrease in ρ due to an increase of carriers
from both electrons and holes.

Semiconductor Theory of
Photoelectrochemistry

It is known that metal electrodes can produce photocurrents when illuminated, and semiconductor electrodes may do likewise, while at the same time generating photovoltages.[4] In an electrolyte solution, the conduction and valence bands of the semiconductor are bent near the surface in a "depletion layer," which will help separate e^-/h^+ pairs and thus make the electrons available for reduction and for oxidation.

Fig. 3. Left: band gap between valence and conduction bands. Right: electrons move from the valence band to the conduction band in an intrinsic semiconductor.
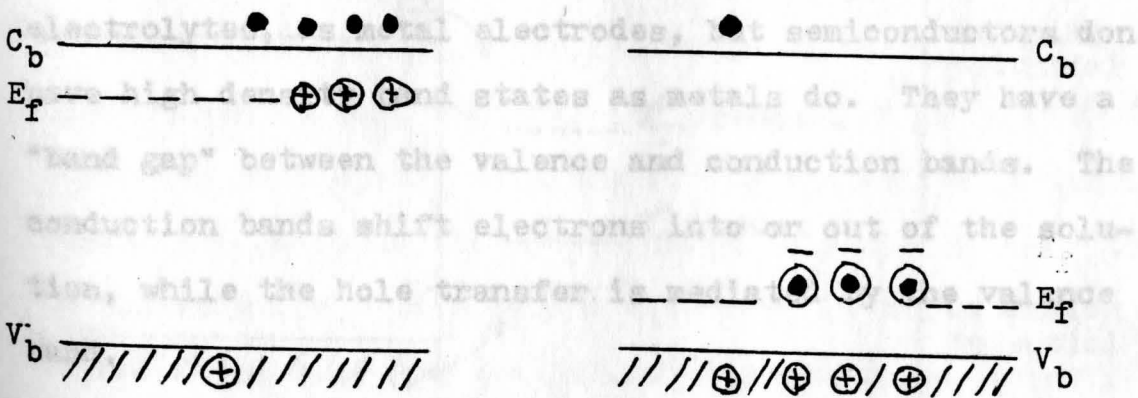
According to Jansen,[5] photoelectrolysis is the result of a photoelectric effect combined with "chemical reactivity." Semiconductor electrodes perform redox chemistry in electrolytes as metal electrodes, but semiconductors don't have high density of band states as metals do. They have a "band gap" between the valence and conduction bands. The conduction bands shift electrons into or out of the solution, while the hole transfer is mediated by the valence

Fig. 4. Left: conduction band populated with electrons from the valence band and the donor state (E_f) of the n-type semiconductor. Right: holes in the conduction band of a p-type semiconductor as a result of electron migration to the conduction band and the acceptor state (E_f).

Electrolysis with solution redox reactions may be represented as follows:

(1)

(2)

where Ox_1, Ox_2, Red_1, and Red_2 are oxidized and reduced species of the redox couple; e^- is the electron from the

Semiconductor Theory of
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Electrolysis with solution redox reactions may be
represented as follows:

$$Ox_1 + e^- = Red_1 \tag{1}$$
$$Red_2 + h^+ = Ox_2 \tag{2}$$

where Ox_1, Ox_2, Red_1, and Red_2 are oxidized and reduced
species of the redox couple; e^- is the electron from the

conduction band; h^+ is the hole of the valence band. When
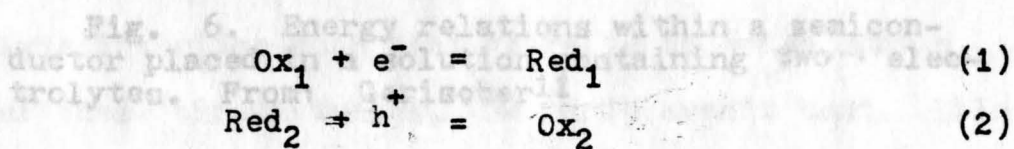a semiconductor is placed in a solution, the chemical poten-
tial of e^- in the semiconductor given by E_f, will differ
from that of the redox couple in solution E_f^o (Figure 6).
What occurs is that the Fermi levels will equilibrate by
transferring majority carriers, usually into the electrolyte.
As equilibrium is attained, there is an accumulation of ions
at the electrode surface, (H^+, OH^-), known as the Helmholtz
layer, and there is usually a charge depletion within the
surface of the semiconductor. In an n-type material, E_f
for the semiconductor is usually above E_f^o, the redox couple
in solution, and electrons move from the semiconductor,
which becomes positive, to the solution. As shown in Fig-
ure 7.

Excess charge isn't on the surface as for a metal,
but in a "space charge" region. This resulting potential is
represented as band bending, indicated in Figure 7. These
bands are bent upward with respect to the bulk of the semi-
conductor, in which the space charge is positive with respect
to the solution. This causes electrons in the space charge
region to move toward the bulk of the semiconductor, and the
holes to rise to the surface.

A potential may be imposed upon the semiconductor/
electrolyte interface and measured, if one becomes zero,
and under these circumstances, the bands aren't bent. This
potential is known as the "flat band potential," (E_{fb}).

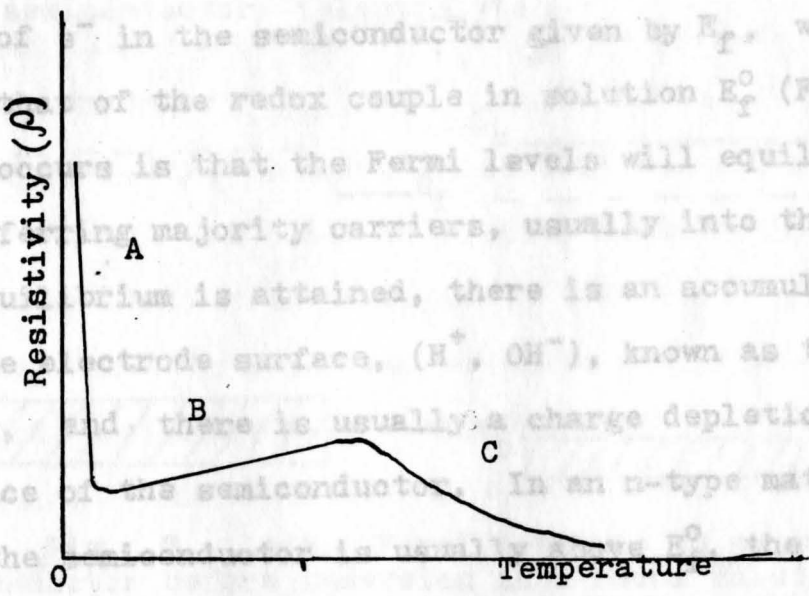It is a unique property of semiconductors, where

Fig. 5. Resistivity of a doped semicon-
ductor as a function of temperture.
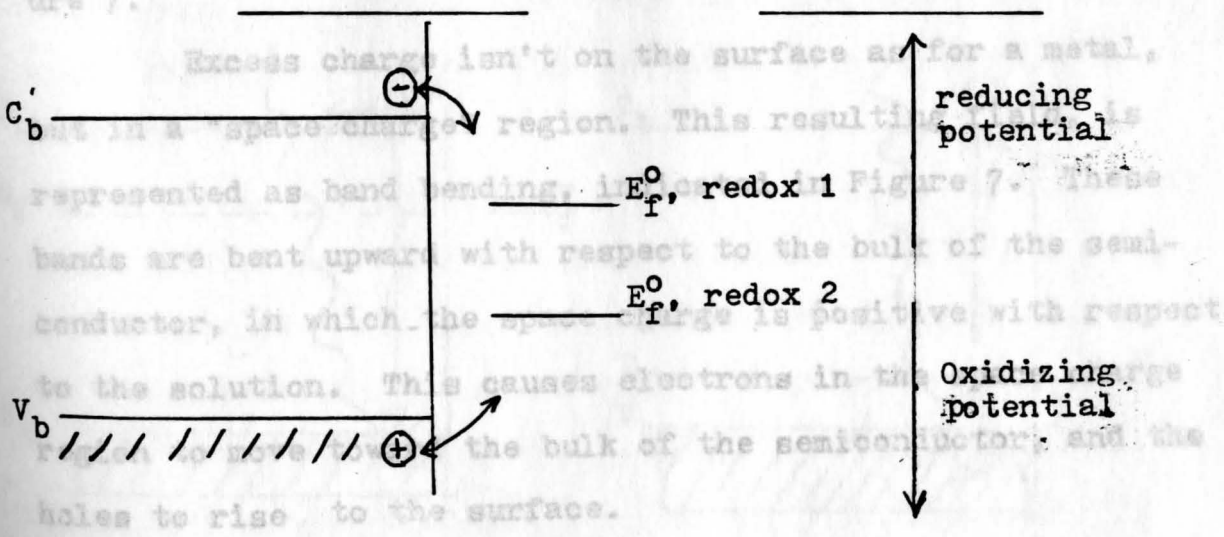
Fig. 6. Energy relations within a semicon-
ductor placed in a solution containing two elec-
trolytes. From: Gerischer[11]

conduction band; h^+ is the hole of the valence band. When a semiconductor is placed in a solution, the chemical potential of e^- in the semiconductor given by E_f, will differ from that of the redox couple in solution E_f^o (Figure 6). What occurs is that the Fermi levels will equilibrate by transferring majority carriers, usually into the electrolyte. As equilibrium is attained, there is an accumulation of ions at the electrode surface, (H^+, OH^-), known as the Helmholtz layer, and there is usually a charge depletion within the surface of the semiconductor. In an n-type material, E_f for the semiconductor is usually above E_f^o, the redox couple in solution, and electrons move from the semiconductor, which becomes positive, to the solution, as shown in Figure 7.

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A potential may be imposed upon the semiconductor/ electrolyte interface such that there is no space charge, and under these circumstances, the bands aren't bent. This potential is known as the "flat band potential," (E_{fb}).

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semiconductor electrolyte

C_b

E_f

C_b

E_f

E_f^o

V_b

V_b
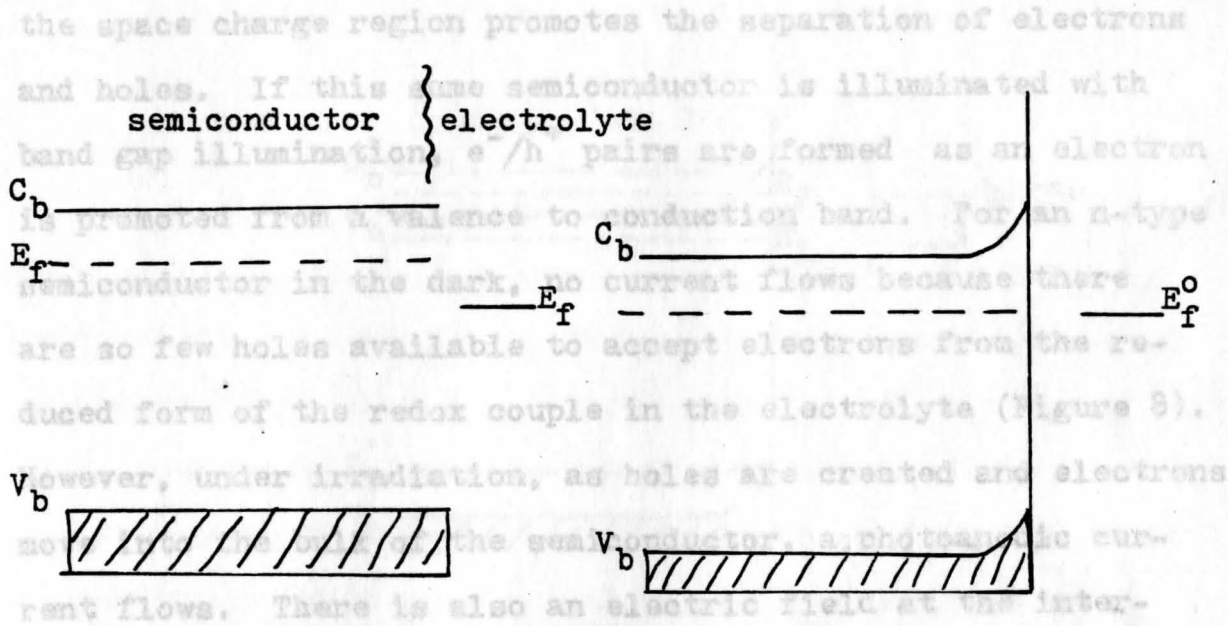
Fig. 7. Left: Fermi level in an n-type semi-
conductor before immersion in a redox solution.
Right: Fermi level after immersion. An electron de-
pletion layer formed within the electrode causing
band bending.

C_b

E_f

C_b

E_f^o

V_b

E_f

V_b

E_f^o
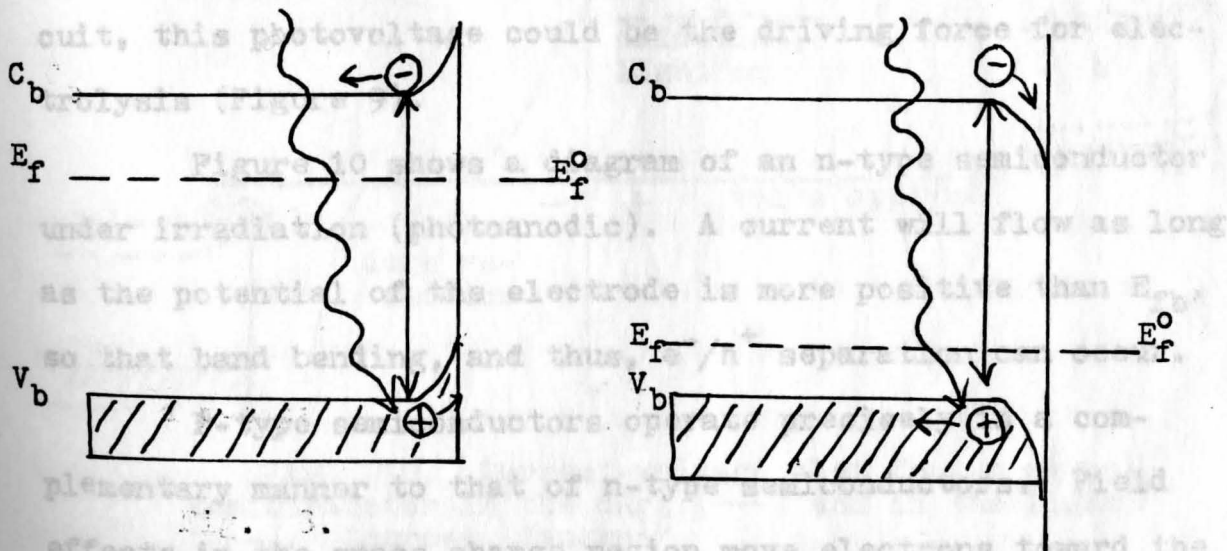
Fig. 8. The effects of illumination in the
depletion layer. Left: the effects at the inter-
face of an n-type semiconductor. Right: the elec-
tric field separates the charge at the interface
of a p-type semiconductro. Source: Gerischer[11]

the space charge region promotes the separation of electrons and holes. If this same semiconductor is illuminated with band gap illumination, e^-/h^+ pairs are formed as an electron is promoted from a valence to conduction band. For an n-type semiconductor in the dark, no current flows because there are so few holes available to accept electrons from the reduced form of the redox couple in the electrolyte (Figure 8). However, under irradiation, as holes are created and electrons move into the bulk of the semiconductor, a photoanodic current flows. There is also an electric field at the interface, causing a shift of the conduction and valence bands upward, diminishing the band bending. The photovoltage is the change in Fermi levels from dark to illuminated conditions, and if a counter electrode were introduced to the circuit, this photovoltage could be the driving force for electrolysis (Figure 9).

Figure 10 shows a diagram of an n-type semiconductor under irradiation (photoanodic). A current will flow as long as the potential of the electrode is more positive than E_{fb}, so that band bending, and thus, e^-/h^+ separation can occur.

P-type semiconductors operate precisely in a complementary manner to that of n-type semiconductors. Field effects in the space charge region move electrons toward the surface and holes toward the bulk (Figure 8), so that p-type materials catalyze photoreductions of redox couples in solution.
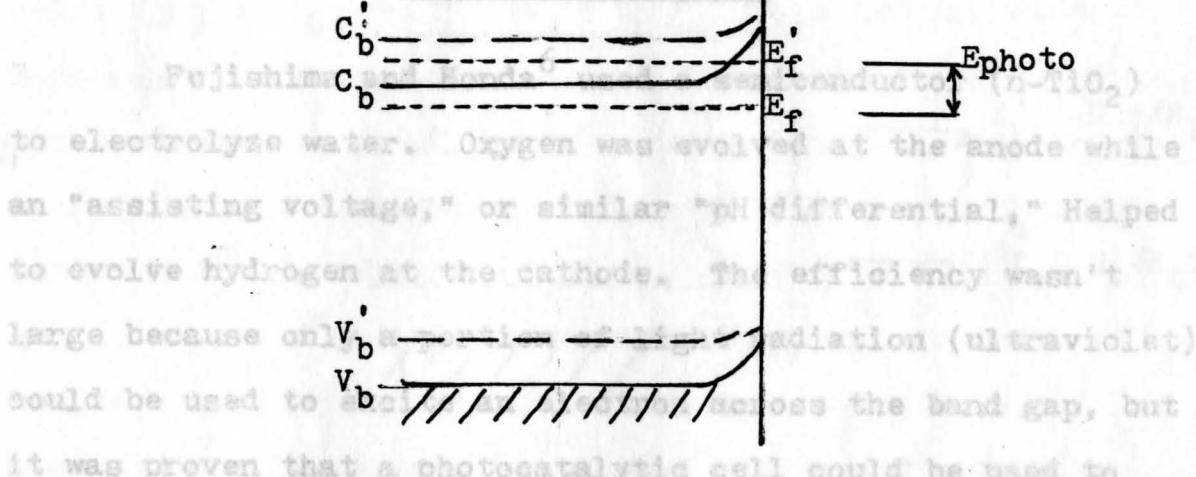
Fig. 9. Illumination produces a counter field which shifts the valence and conduction band upward in the n-type semiconductor. Photovoltage, (E_{photo}), is the change in Fermi level. Source: Gerischer[12]
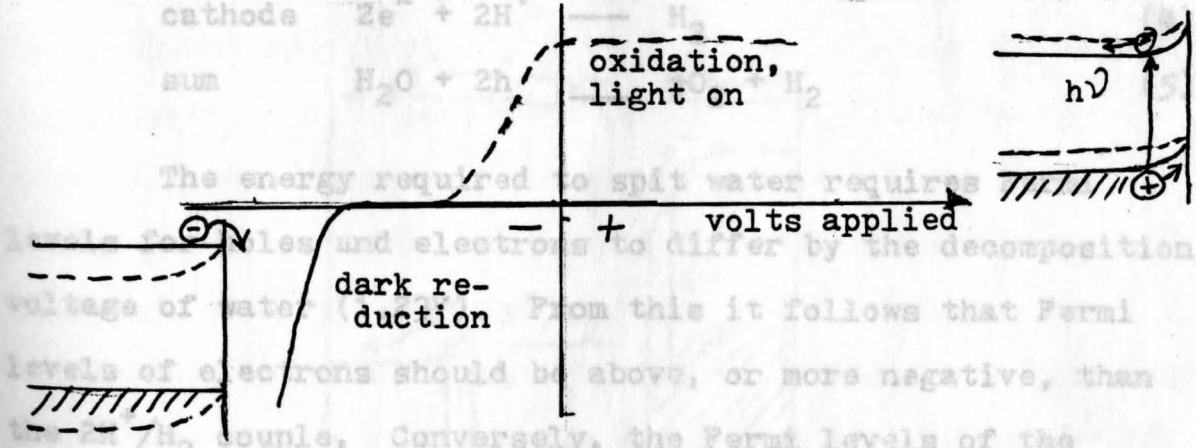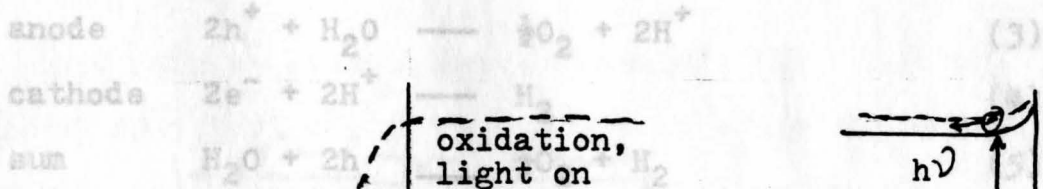

Fig. 10. Current-voltage plot for an n-type semiconductor in the dark (——) and in the light (---). Source: Janzen[10]

Water Decomposition

Fujishima and Honda[6] used a semiconductor (n-TiO_2) to electrolyze water. Oxygen was evolved at the anode while an "assisting voltage," or similar "pH differential," Helped to evolve hydrogen at the cathode. The efficiency wasn't large because only a portion of light radiation (ultraviolet) could be used to excite an electron across the band gap, but it was proven that a photocatalytic cell could be used to split water.

The reactions could be summarized as follows:

anode	$2h^+ + H_2O$	—— $\frac{1}{2}O_2 + 2H^+$	(3)
cathode	$2e^- + 2H^+$	—— H_2	(4)
sum	$H_2O + 2h$	—— $\frac{1}{2}O_2 + H_2$	(5)
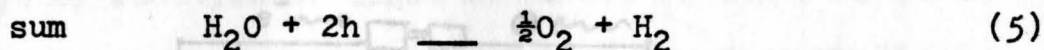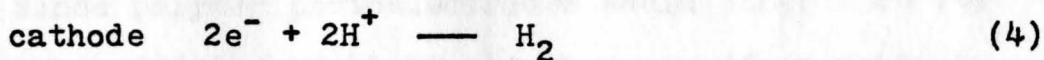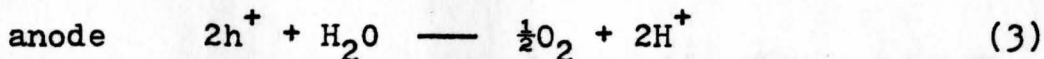
The energy required to spit water requires Fermi levels for holes and electrons to differ by the decomposition voltage of water (1.23V). From this it follows that Fermi levels of electrons should be above, or more negative, than the $2H^+/H_2$ couple, Conversely, the Fermi levels of the holes should be below, or more positive, than the H_2O/O_2 couple (Figure 11). Therefore, illumination has to be sufficiently energetic to split Fermi levels of the holes and electrons by more than the decomposition voltage, which would be the minimum energy requirement.

Most semiconductors have too large a band gap to absorb visible light, or are unable to decompose water because Fermi levels can't split enough to cause evolution of hydrogen and oxygen. To overcome this deficiency, Nozik[7] suggested placing two semiconductor photoelectrodes in series--an n-type for O_2 evolution, and the p-type for hydrogen production. The electrodes could produce additive photovoltages to increase the "overall cell efficiency" as shown in Figure 12. This arrangement of two photoelectrodes in series mimics the natural arrangement of Photosystems I and II in chloroplasts.

Fig. 11. Diagram of the minimum conditions for the decomposition of water.

Statement of the Problem

Since polymer photoelectrodes would offer more versatility, by addition of light absorbers or other conducting polymers, to harness more useful energy from sunlight, they could conceivably overcome the problems inherent in semiconductors. It was desired to construct a monomer of acetylene attached to a dye molecule, (Chrome Azurol S, Figure 14), which when polymerized would mimic a p-type semiconductor. The photoelectrode would be used to catalyze the decomposition of water when immersed in an electrolyte.

The desired monomer will consist of a propargyl group, ($CH \equiv C-CH_2-$), and the dye moiety (Chrome Azurol S). The route of organic synthesis employed the Williamson ether synthesis (Figure 15). It entailed a substitution reaction whereby a halogen is substituted by a phenoxide of the

Fig. 12. An n-p photoassisted system.

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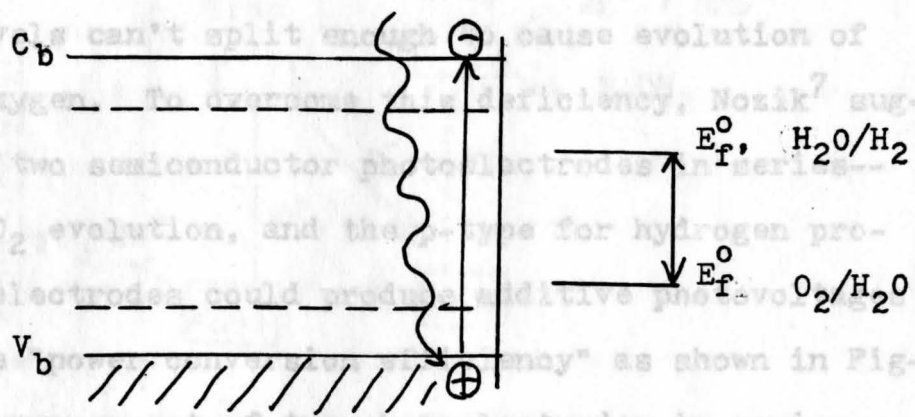
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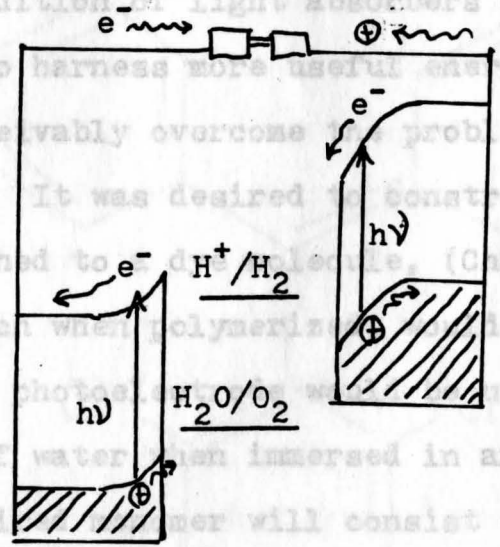
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dye to form the monomer, by a stable ether linkage.[8]

The synthesized polymer, polyacetylene, poly(CH), is to be conductive while the organic dye would branch off the polymer as a "pendent" group, and be necessary to create an electrical gradient for separating charge and producing a chemical potential when irradiated.

When a p-type semiconductor is immersed in an electrolyte, the majority current carriers (holes) leave the surface of the semiconductor and enter the solution to balance the ... depletion layer ... create ... at the surface of the semiconductor where light is absorbed. The depletion layer will act as a barrier against the further loss of holes, which is reflected by bending of the valence and conduction bands near the surface. This forms the charge gradient in which e^-/h^+ pairs by band gap illumination are separated, leading to photoelectrochemistry.

In the "p-type" dye doped polymer, the Chrome Azurol S moiety has three Na+ counter ions. When immersed in an aqueous solution, the loss of Na+ creates the charge gradient which will separate e^-/h^+ pairs created by absorption of light corresponding to the band separation of the characteristic dye.

I wish to acknowledge Dixon,[9] Janzen,[10] and Gerlanner[11] for the sections on theory. ... p-type dye doped polymer is due to Mettee.[11b]

Fig. 13. Photosystems I and II are mimicked by n- and p-type semiconductors in water splitting.

Fig. 14. Structure of Chrome Azurol S.

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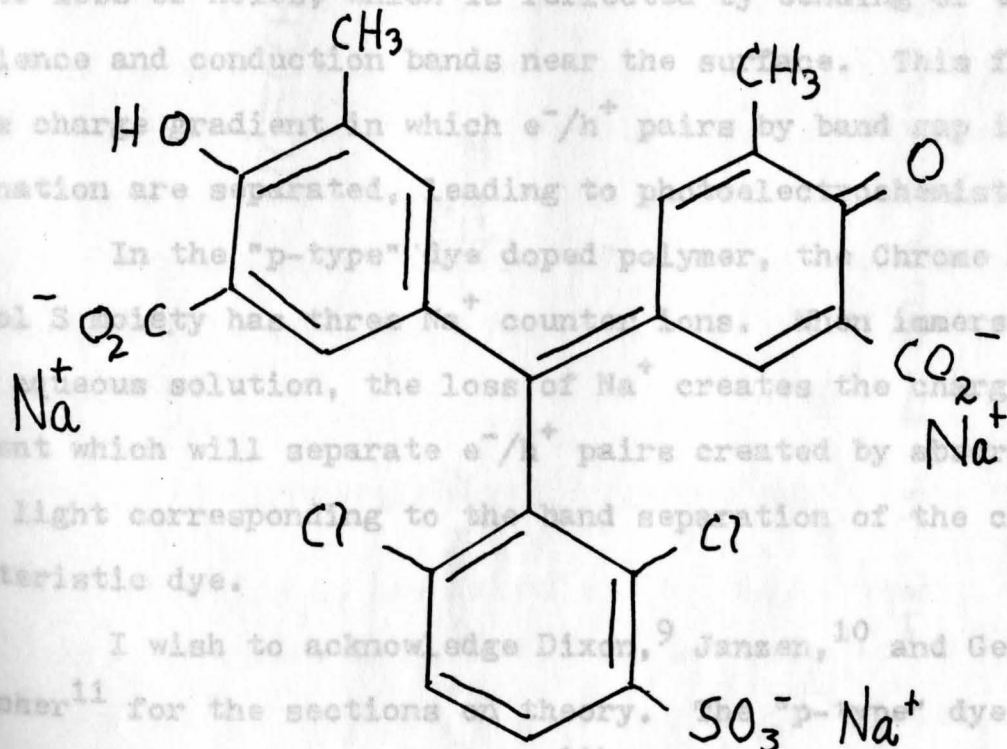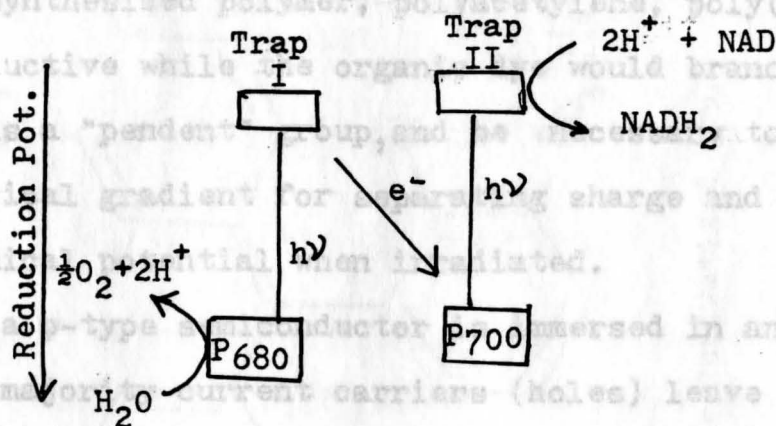When a p-type semiconductor is immersed in an electrolyte, the majority current carriers (holes) leave the surface of the semiconductor and enter the solution to balance the Fermi levels. A depletion layer is created at the surface of the semiconductor where light is absorbed. The depletion layer will act as a barrier against the further loss of holes, which is reflected by bending of the valence and conduction bands near the surface. This forms the charge gradient in which e^-/h^+ pairs by band gap illumination are separated, leading to photoelectrochemistry.

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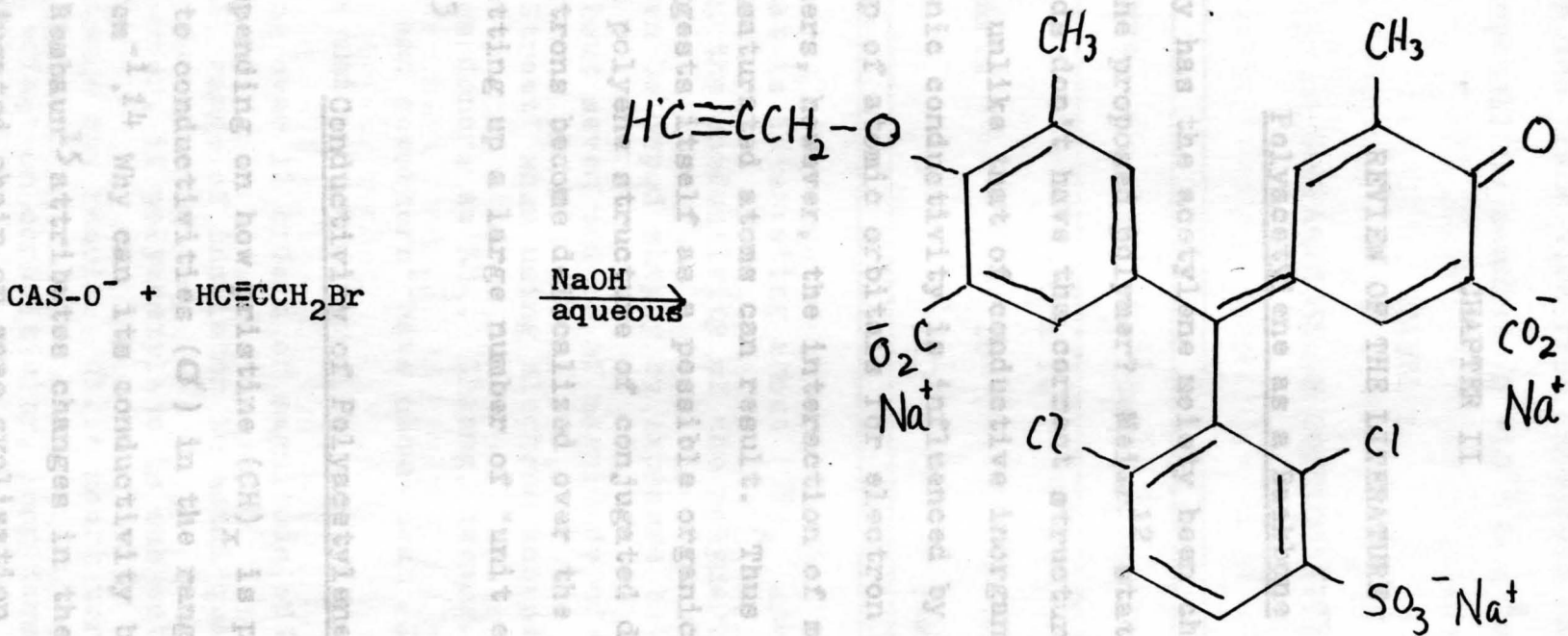
$$\text{CAS-O}^- + \text{HC} \equiv \text{CCH}_2\text{Br} \xrightarrow[\text{aqueous}]{\text{NaOH}}$$

Fig. 15. The Williamson ether synthesis and the derivatized dye.

CHAPTER II

REVIEW OF THE LITERATURE

Polyacetylene as a Backbone

Why has the acetylene moiety been chosen as the backbone for the proposed polymer? Meier[12] states that most organic solids don't have the correct structure for electron transport, unlike that of conductive inorganic solids, whereby electronic conductivity is influenced by close packing and overlap of atomic orbitals for electron exchange. In some polymers, however, the interaction of molecular orbitals of unsaturated atoms can result. Thus polyacetylene, $(CH)_x$, suggests itself as a possible organic conductor. $(CH)_x$ is a polyene structure of conjugated double bonds. The π electrons become delocalized over the whole structure, thereby setting up a large number of "unit electronic conductors."[13]

Conductivity of Polyacetylene

Depending on how pristine $(CH)_x$ is prepared, it can give rise to conductivities (σ) in the range of 10^{-12} to 10^{-6} ohm^{-1}cm^{-1}.[14] Why can its conductivity be varied so greatly? Rembaum[15] attributes changes in the interruptions in the conjugated chain or some cyclization in the $(CH)_x$ chain. Hatano[16] and associates state that conductivity will

increase in the transition from amorphous (σ=10^{-9}-10^{-12} ohm^{-1} cm^{-1}) to crystalline samples (σ =10^{-5} ohm^{-1}cm^{-1}).

TABLE 1

COMPARISONS OF CONDUCTIVITY

Structure	σ (ohm^{-1}cm^{-1})	Type
Cu	6×10^5	conductor
Fused quartz	10^{-16}	insulator
CuO	10^{-5}	semiconductor

What is interesting about (CH)$_x$ are the effects doping has on the conductivity of the polymer. Polymer films of (CH)$_x$ can be doped simply by exposure to Br$_2$ or I$_2$ for example. About seven orders of magnitude of σ have been observed by Street[17] when using electron acceptors such as BF$_3$ and electron donors as NH$_3$. Chiang, Heeger, MacDiarmid, Shirakawa, and coworkers[18] have shown that (CH)$_x$ can be doped with donors and acceptors to yield n-type and p-type materials ranging over 12 orders of magnitude of σ. This represents a full range of insulator to metal qualities.

However, if polyacetylene is subjected to air, irreversible damage may result. While short term exposure has a positive effect on conductivity, long term exposure to oxygen reduces conductivity irreversibly through peroxide formation and hydroxylation of double bonds.[19]

Theory of Conductivity in $(CH)_x$

The mechanism of conductivity in $(CH)_x$ has been in-completely known for many years, and recently Chien[20] intro-duced a unifying concept taken from solid state physics called the "soliton" theory. Chien uses the soliton, a free radical, to interpret the effects of isomerization, doping, and electrical conductivity and uses EPR data as evidence of unpaired spins. Polyacetylene, depending how it is pre-pared, exists in three isomeric structures. (Figure 16)

When $(CH)_x$ is prepared at $-70^{\circ}C$ it shows no EPR signal. The predominant structure at this temperature is the cis-transoid configuration. It is inferred that the valence band of the π orbital is filled while the con-duction band isn't occupied. As thermal energy is intro-duced, there is an EPR signal resulting from an isomer-ization effect between cis and trans portions of $(CH)_x$ as the long and short bonds of the polymer interchange cre-ating the unpaired state.

Chien defines the soliton domain, as where an unpaired spin, or free radical, exists (Figure 17). The domain is formed because there is a change in the phase of the π wave function. The soliton, $(S^{\cdot})$, exists in the center of the domain. This symbol is that of a neutral soliton (charged solitons, $S^{\pm}$, also exist). It must be noted that the neutral soliton isn't a fixed entity, but can traverse the $(CH)_x$ molecule.

Fig. 17. Defects caused by the soliton domain.

cis-transoid

trans-cisoid

trans-transoid

Fig. 16. Isomeric forms of $(CH)_x$.

These migrations set up what is known as annihilation, where
there is interaction between the unpaired spins. (Figure 18)

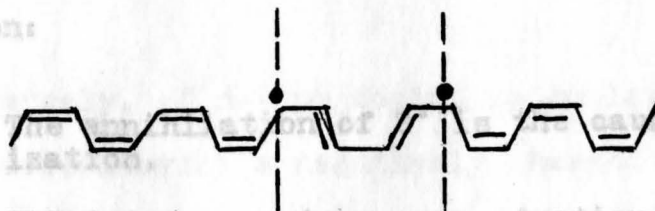Summarizing what Chien's hypothesis says regarding
isomerization:

1. The annihilation of S• is the cause of isomer-
ization.

2. EPR data suggests a concentration of about
one S• per (CH)$_x$.

Fig. 17. Defects caused by the soliton domain.

3. The S• is mobile at room temperature, with its
mobility decreasing with temperature. The S•
in (CH)$_x$ at -70°C, (cis form).

Regarding the method of conduction in polyacetylene,
it is sure the soliton itself isn't the current carrier. Pol-
yacetylene is a p-type semiconductor at room temperature, in
that the carrier is positively charged. Therefore, the role
of the soliton is to cause the formation of h• carriers.[21]
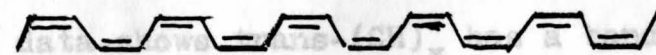Experimental data shows that cis-(CH)$_x$ has a band gap of 1.5 eV,
and it postulated by Chien that solitons are nonbonding elec-
trons and exist somewhere within this band gap. Therefore,

Fig. 18. Migration of solitons and their annihil-
ation.

it is possible to create holes when electrons leave the lower
lying valence band to populate the higher soliton level.

P-type and n-type dopants have also been handled
with the soliton theory. In the first case, p-type dopants,
the dopant oxidizes S• and converts it to a delocalized
carbonium ion. The paramagnetic S• is converted to a spin-
less soliton, (S+). Also, it was postulated that the poly-
chain could be oxidized, giving rise to a cation radical.
The π kink is still maintained in this structure as Fig-

These migrations set up what is known as annihilation, where there is interaction between the unpaired spins. (Figure 18)

Summarizing what Chien's hypothesis says regarding isomerization:

1. The annihilation of S· is the cause of isomerization.

2. EPR data suggests a concentration of about one S· per $(CH)_x$.

3. The S·is mobile at room temperature, with its mobility decreasing with temperature. The S· in $(CH)_x$ at $-70°C$, (cis form).

Regarding the method of conduction in polyacetylene, it is sure the soliton itself isn't the current carrier. Polyacetylene is a p-type semiconductor at room temperature, in that the carrier is positively charged. Therefore, the role of the soliton is to cause the formation of h^+ carriers.[21] Experimental data shows trans-$(CH)_x$ has a band gap of 1.5 eV, and it postulated by Chien that solitons are nonbonding electrons and exist somewhere within this band gap. Therefore, it is possible to create holes when electrons leave the lower lying valence band to populate the higher soliton level.

P-type and n-type dopants have also been handled with the soliton theory. In the first case, p-type dopants, the dopant oxidizes S· and converts it to a delocalized carbenium ion. The paramagnetic S· is converted to a spinless soliton, (S^+). Also, it was postulated that the polychain could be oxidized, giving rise to a cation radical. The π kink is still maintained in this structure as Fig-

ure 19 shows. Both of these processes occur simultaneously, and depend on the types of acceptors used. The changes are viewed with EPR as increase, decrease, or no net change in the EPR.

Conversely, if n-type doping is employed, reduction of the S· occurs leaving a negatively charged soliton, (S⁻). If reduction takes place on the polymer chain a radical anion is formed (Figure 20).

Chien's last statement pertains to conduction. He notes that conduction of doped $(CH)_x$ is the result of carrier rather than charge transfer. These results were concluded from work done with conductivity and thermopower, (Γ), in doped $(CH)_x$.

Fig. 20. (Top); Reduction occurs at the S·
forming a delocalized carbanion. (Bottom), Reduc-
tion elsewhere in the polymer forming a radical
anion. (where ═ = C═C and — = C-C)

CHAPTER III

EXPERIMENTAL

Fig. 19. (Top), The dopant oxidizes S· directly forming a carbenium ion. (Bottom), The dopant oxidizes the polymer chain directly forming a cation radical. (where ▬ = C=C and — = C-C)
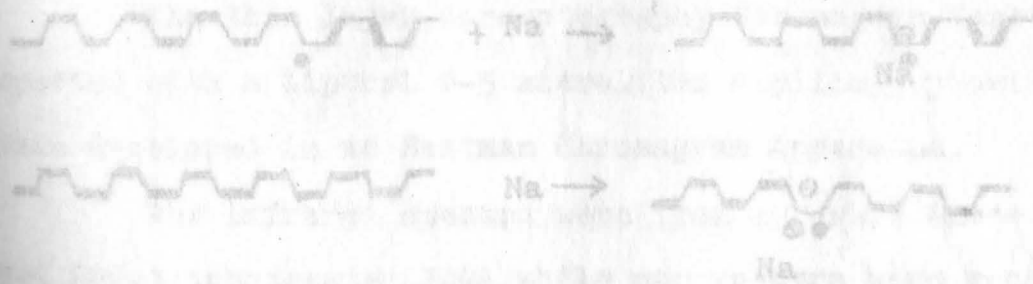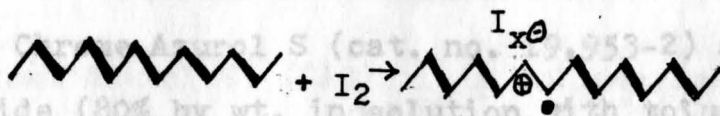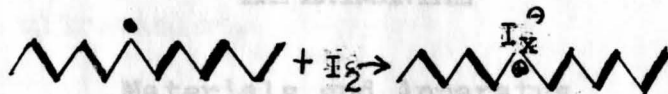

Fig. 20. (Top), Reduction occurs at the S·· forming a delocalized carbanion. (Bottom), Reduction elsewhere in the polymer forming a radical anion. (where ▬ = C=C and — = C-C)

CHAPTER III

EXPERIMENTAL

Materials snd Apparatus

The Chrome Azurol S (cat. no. 19,953-2) and pro-
pargyl bromide (80% by wt. in solution with toluene for
stabilization; cat. no. P5,100-1) was purchased from the
Aldrich Chemical Company, Milwaukee, Wisconsin. Deuterium
oxide (99.8% atom D) came from Aldrich also. Potassium
bromide and sodium sulfate were analytical grade Baker
Analyzed Reagents. Chloroform and acetic acid were from
Fisher Scientific. Ethanol and n-butanol came from Mallin-
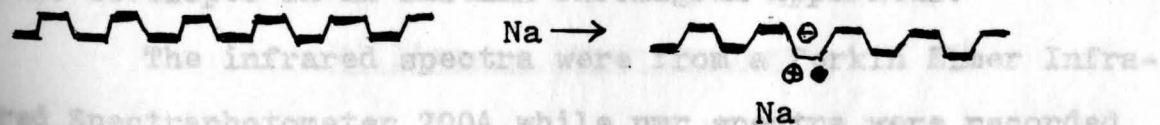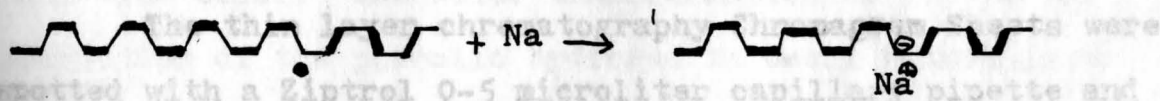ckrodt. All water was either distilled or deionized.

The thin layer chromatography Chromagram Sheets were
spotted with a Ziptrol 0-5 microliter capillary pipette and
were developed in an Eastman Chromagram Apparatus.

The infrared spectra were from a Perkin Elmer Infra-
red Spectraphotometer 700A, while nmr spectra were recorded
on a Varian Anaspect EM-360 (60 MHz).

Cyclic voltammetry required an EG&G Princeton
Applied Research (Model 364) Polaragraphic Analyzer, a Val-
tec (Model 1024) x-y Recorder, and a Sabtronics (Model
2010A) Multimeter to follow the potential. The Wavetek
(Model 142) HP VCG Generator was employed for the sawtooth
wave needed in cyclic voltammetry.

The illumination source was a 1000W mercury-xenon arc lamp, by Hanovia Lamp Division, filtered by 10 cm of water to remove the infrared. The radiation consisted of visible and ultraviolet.

Chemistry of Chrome Azurol S

Chrome Azurol S, (CAS), is a triphenylmethane type dye derivative that is quite soluble in water. Its ionic character is contributed by three acidic functions, in addition to the phenolic hydrogen. Two of the acidic functions are carboxylate while the third is a sulfonate group (Figure 14).

One important property of this dye was its pH/color dependence. In acidic and neutral aqueous solutions, the dye has a deep red color. In basic solutions, CAS takes on a deep blue color. The color transformation is due to the ionization of the phenolic hydrogen in basic solution, as shown in Figure 21.

Williamson Ether Synthesis

CAS (2g) was added to an aqueous solution (50 ml) of sodium hydroxide (0.3g) in a three necked round bottom flask. Propargyl bromide (1 ml) was added to the aqueous solution and refluxed for 2 hours (Figure 22). The reaction mixture was kept below 80°C so the propargyl bromide wouldn't polymerize. Intially, the solution was a deep blue color, indicative of the phenoxide ion present. During the refluxing, the pH was monitored periodically so that conditions
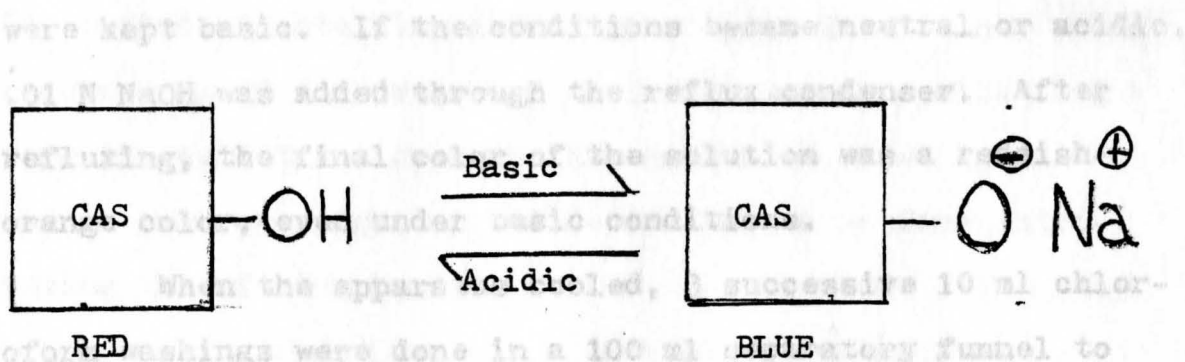
Fig. 21. The color transformation of CAS is due to the phenolic hydrogen. In basic conditions, the hydrogen is lost and the phenoxide is formed. Acidity provides attachment of the hydrogen back onto CAS.

Fig. 22. The apparatus for the Williamson Ether Synthesis.

were kept basic. If the conditions became neutral or acidic, .01 $\underline{N}$ NaOH was added through the reflux condenser. After refluxing, the final color of the solution was a reddish-orange color, even under basic conditions.

When the apparatus cooled, 3 successive 10 ml chloroform washings were done in a 100 ml separatory funnel to remove the unreacted propargyl bromide. The aqueous layer was transferred to a Büchner funnel and suction filtered to remove any residue. The product, in aqueous solution, was flash evaporated with a cold trap/ vacuum pump system at 5-10 torr. The final product was an orange powder. It was quite different in color from the red crystals of CAS.

Thin Layer Chromatography

TLC was performed to show that the CAS starting material could be separated from the propargyl-coupled monomer, since they have such closely related structures. A TLC Eastman Chromagram sheet, of silica gel G, was spotted with a 5 microliter sample of the CAS and the monomer. The samples were developed for 2 hours, during which time the samples travelled 4.5 to 5.5 cm. The solvent system employed a 60:20:10:10 of n-butanol, acetic acid, ethanol, and water, as described by Venkataraman.[22]

Infrared Data

The ir background of pure KBr is limited to a few easily identified bands, which was the reason for choice.

The method of obtaining a KBr pellet came from Stine.[23] It required a 30 ton press and a die to cast the pellet. Before the pellet was cast the KBr had to be dried in a vacuum oven overnight at $110^{\circ}C$, to keep water from introducing interfering bands.

Nuclear Magnetic Resonance

Since CAS and the monomer were soluble, deuterium oxide was chosen as the solvent. TMS was used as an external standard because of its insolubility in water.

Cyclic Voltammetry

Cyclic voltammetry (CV) was employed as a method to electropolymerize the monomer. Generally, CV can be used to detect any chemical species that is electroactive, i.e., that can undergo redox chemistry. In this technique, the potential of the working electrode is the controlled parameter, which causes a chemical species near the electrode to be oxidized or reduced.

The potential can be interpreted as an "electron pressure" which forces a species into solution to gain e^- (reduction) or lose e^- (oxidation). As the potential of the electrode becomes more negative, it becomes more strongly reducing. Likewise, the more positive the electrode becomes, the more oxidizing it is.

The current (i) is a measure of the amount of electron flow. When a reaction occurs at the electrode, this

current is proportional to the concentration of the electro-active species near the electrode. A cathodic current is usually assigned a positive sign, and that due to oxidation a negative value. If the electrode potential is swept from negative to positive, and a negative current is noted, the current is referred to as an "anodic wave," (Figure 23).

The CV cell was a triple compartment, Pyrex H-type cell whose sections were separated by glass frits. Quartz windows were placed on two of the compartments for photo-chemical work. The platinum electrode was the working electrode, while the counter electrode was silver. The third, a reference electrode, (SCE), was used to refer the working electrode voltage to.

Aqueous .1 $\underline{N}$ Na_2SO_4 was employed as the electrolyte, whose usable window was measured between -.58V to +1.14V. Outside these limits, water will either be oxidized or reduced.

Electrolyte solutions of CAS, propargyl bromide, and the monomer were measured first to determine if any differences in their voltammograms existed. Different scan rates were used for the voltammograms of the monomer solution to determine if currents were a surface attached or a dis-solved species. A fixed voltage experiment was run at 1.15V for 2 hours, to form a film, and then subjected to CV. Finally, the 1000W power supply was employed to measure any photo-electrochemical effects.

CHAPTER IV

RESULTS AND DISCUSSION

Monomer Evidence

Williamson Ether Synthesis

The color changes of the solution in the Williamson synthesis were helpful. The initial deep blue solution indicated the phenoxide needed for the coupling reaction was present. Subsequently, the solution became a reddish-orange, like that of protonated CAS, indicating the coupling of a nonconjugated group to phenoxide.

Except for the ether linked acetyl linkage, the only other modes of attachment would have been an ester linkage between the propargyl group and one of the acidic functions. Morrison and Boyd[24] note that acidic conditions are required for this esterification, and furthermore, hydrolysis of an ester often occurs under warm acidic or basic conditions.

Fig. 23. A cyclic voltammogram illustrating the positions of the cathodic wave(swept left to right), and the anodic wave(swept right to left).

only alteration between CAS and the derivatized dye is that an ether linkage would have replaced the phenolic hydrogen in CAS. Qualitative TLC plates showed that a compound in addition to CAS was present. A new yellow pigment, presumed to be the derivatized monomer, was spotted above

CHAPTER IV

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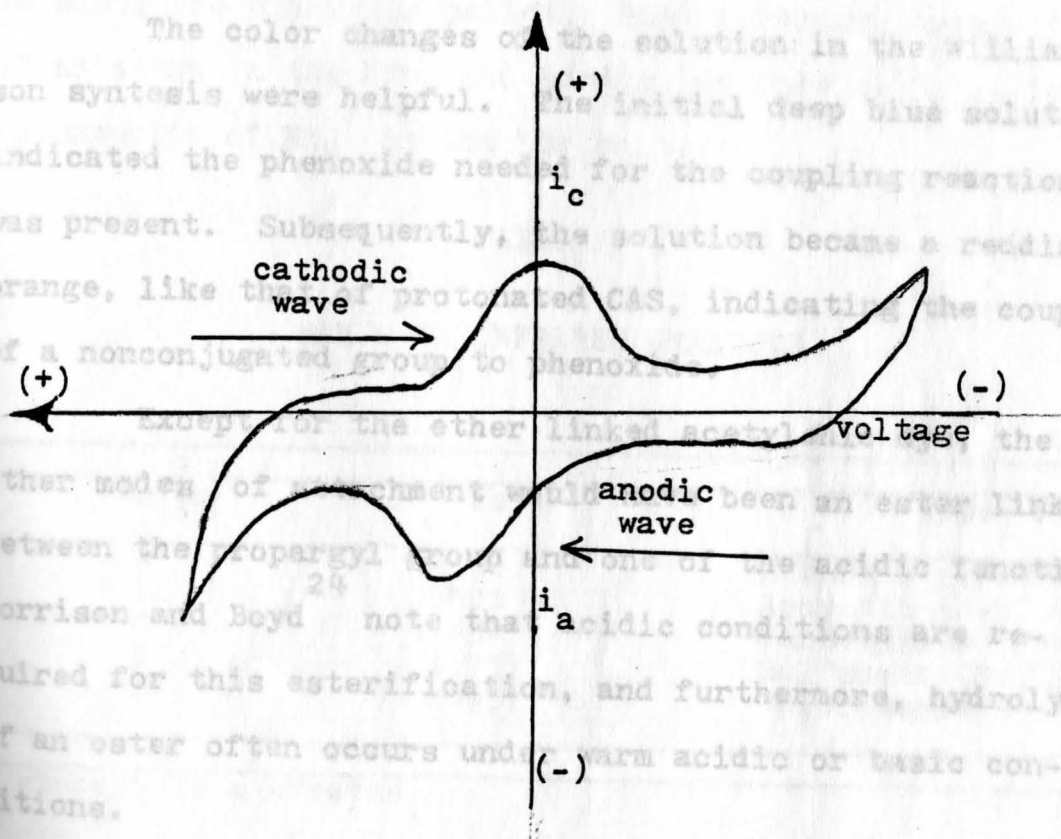ditions.

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nolic hydrogen in CAS. Qualitative TLC plates showed that
a compound in addition to CAS was present. A new yellow pig-
ment, presumed to be the derivatized monomer, was spotted above

the CAS red pigment on the silica layer.

Infrared Data

The KBr pellet proved to be essential in ident-
ifying the groups of the CAS, but evidence of the acetylenic
triple bond could not be established. The use of Silver-
stein[25] was employed in identifying the spectra. Figure
24 shows the blank KBr pellet. Band A results from a trace
of moisture in the KBr, and band B, at 1420 cm^{-1}, is from
an impurity of NH_4^+ in the KBr salt.

TABLE 2

BANDS IN INFRARED ANALYSIS

Region	cm^{-1}	Type
A	3500	Phenolic (O-H) S
B	3000	Aromatic (C-H) S
C	1650	Carboxylate (C=O) S
D	1175	Sulfonate (S=O) S
E	1095	Chlorobenzene

where S is a stretch

The ir spectrum of CAS helped confirm the presence
of substituent groups of the carboxylate, sulfonate, and
chlorobenzene as shown in Figure 25. The ir of the deriva-
tized CAS didn't reveal the presence of an acetylenic group,
however, (2140-2190 cm^{-1}). The weakness of all the bands
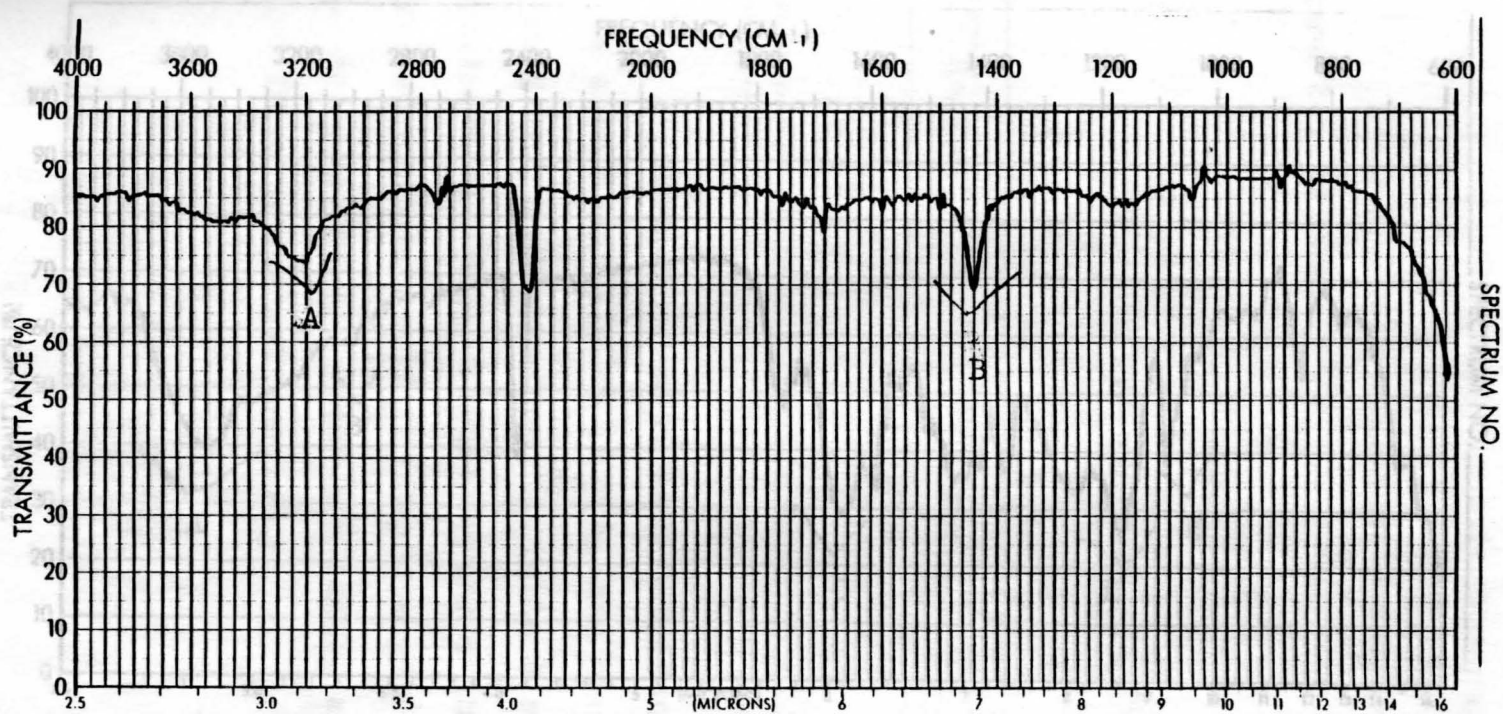in the monomer spectrum may have precluded seeing the (HC≡C-)
group.

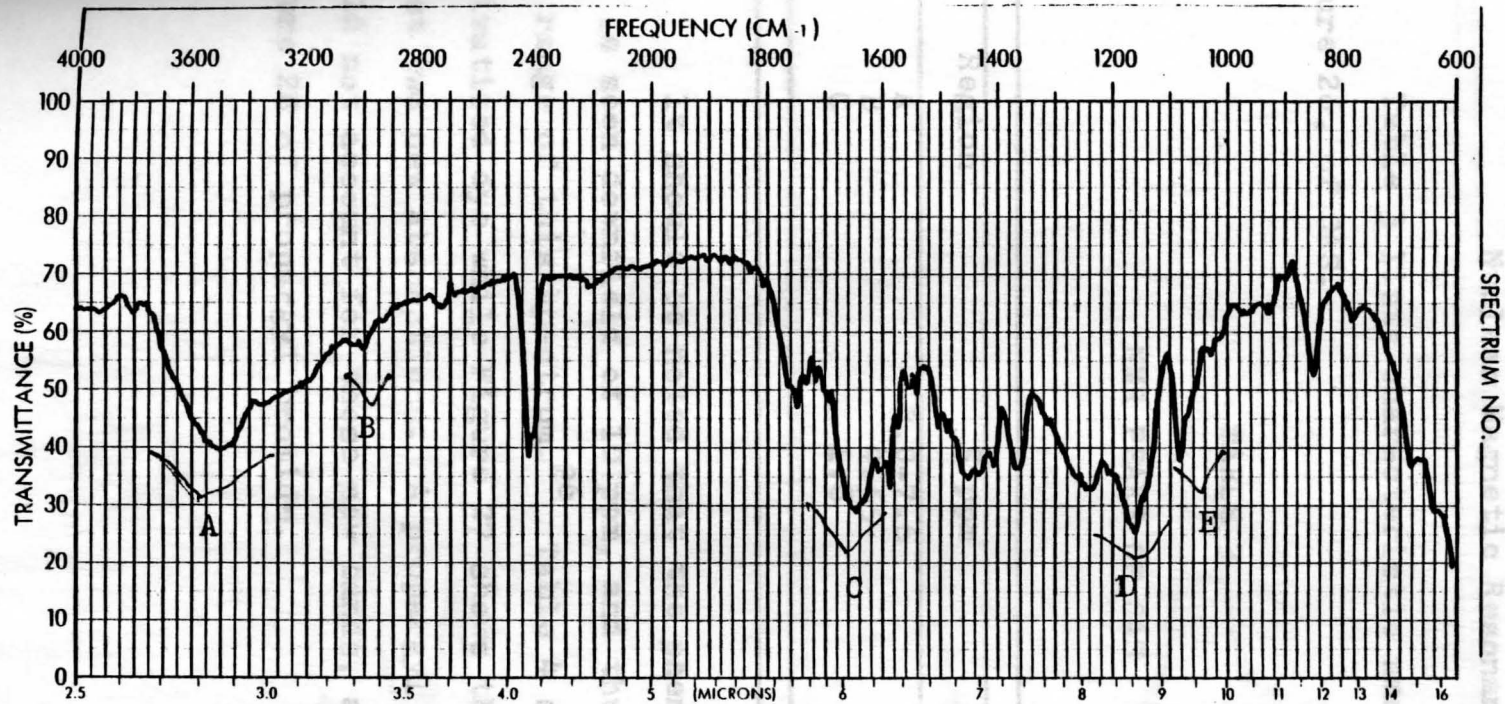Fig. 24. ir spectrum of KBr pellet, (blank).

Fig. 25. ir spectrum of CAS.

Nuclear Magnetic Resonance

Table 3 lists characteristic nmr peaks as shown in Figure 26, of CAS.

TABLE 3

NMR PEAKS OF CAS

Region	δ ppm	Type
A	7.0-7.6	Ar H
B	4.55	H_2O (impurity)
C	1.8	$-CH_3$

It should be noted that the phenolic hydrogen of CAS is seen downfield of 10 ppm, and thus, isn't within the range of this spectrum.[26] Table 4 shows the nmr of the derivatized dye while Figure 27 shows the inclusion of at least two new absorptions. A propargyl bromide impurity would not account for these new bands, as can be seen in Figure 28 of propargyl bromide.
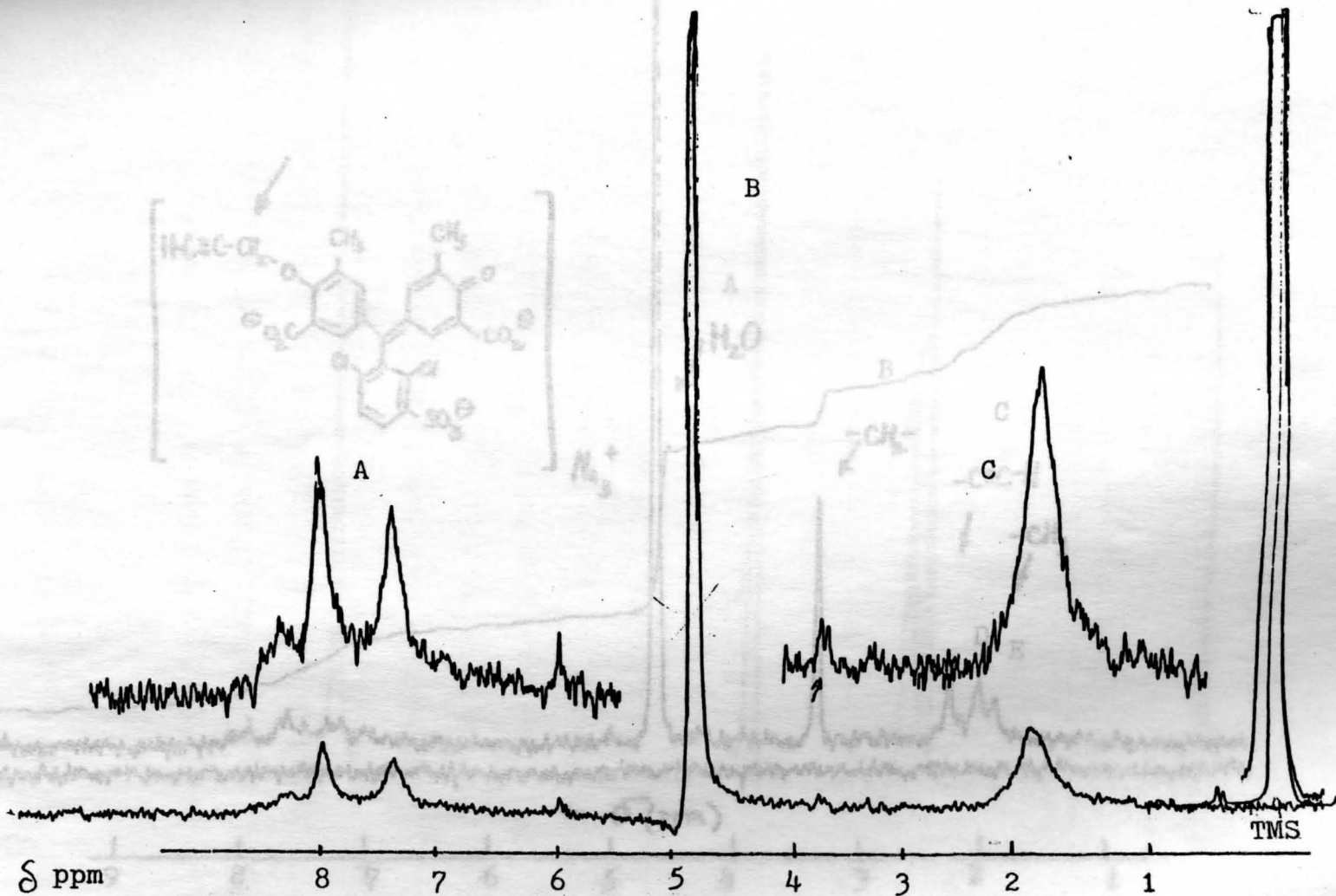
Fig. 26. nmr spectrum of CAS. (Structure in upper left).

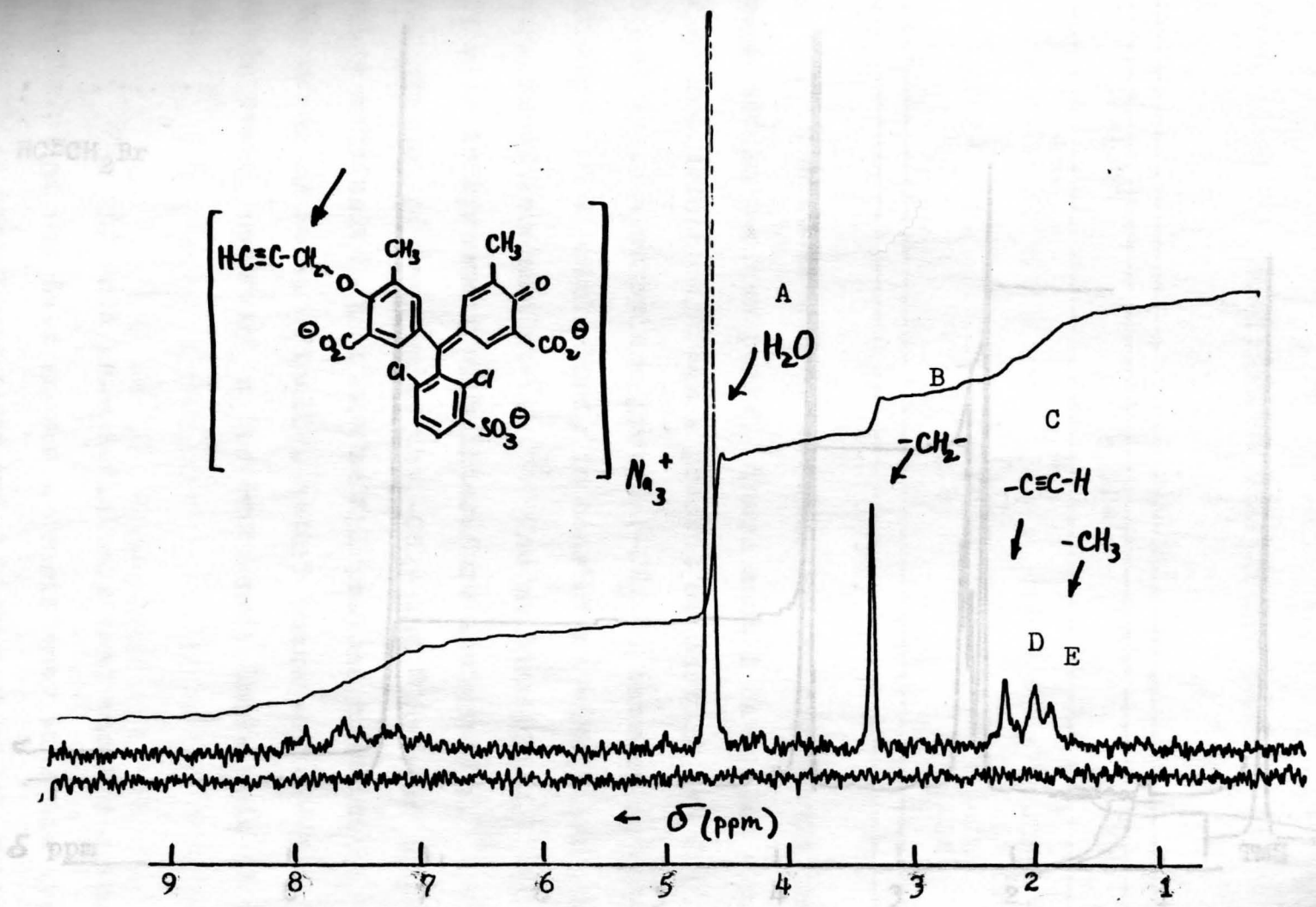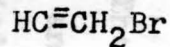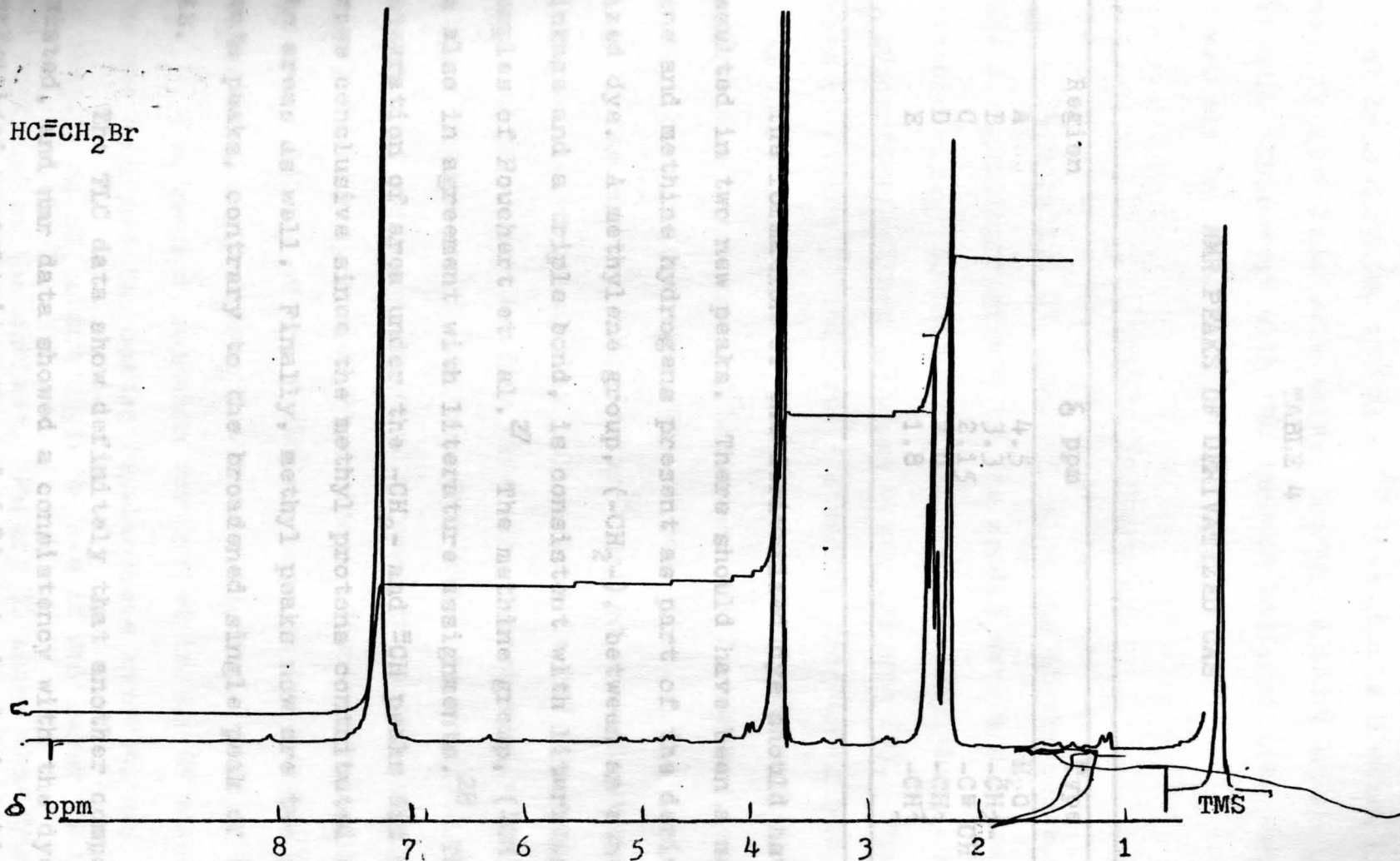Fig. 27. nmr spectrum of monomer. (Structure in upper left).

Fig. 28. nmr spectrum of propargyl bromide. (structure is in above left corner)

TABLE 4

NMR PEAKS OF DERIVATIZED CAS

Region	δ ppm	Type
A	4.5	H_2O
B	3.3	$-CH_2-$
C	2.15	$-C \equiv CH$
D	2.0	$-CH_3$
E	1.8	$-CH_3$

The formation of the derivatized dye should have resulted in two new peaks. There should have been a methylene and methine hydrogens present as part of the derivatized dye. A methylene group, $(-CH_2-)$, between an ether linkage and a triple bond, is consistent with literature samples of Pouchert et al.[27] The methine group, $(\equiv CH)$, is also in agreement with literature assignments.[28] The integration of area under the $-CH_2-$ and $\equiv CH$ peaks did not prove conclusive since the methyl protons contributed to the areas as well. Finally, methyl peaks now are two separate peaks, contrary to the broadened single peak of the CAS.

The TLC data show definitely that another compound existed, and nmr data showed a consistency with the dye derivatized acetylenic compound. Direct chemical evidence of a triple bond in the derivatized CAS was obtained using

a test from Morrison and Boyd.[29] Acetylenic H atoms are
known to give insoluble silver acetylide under acidic con-
ditions. This test with the monomer was positive, whereas
it was not for CAS.

Cyclic Voltammetry

Generally, CV scans of solutions of the monomer
show a significant growth of the anodic wave and a decreasing
cathodic wave. Solutions of CAS and propargyl bromide show
no evidence of either of these waves (Figure 29). The re-
sults of Figure 30 indicate a steadily increasing conduct-
ivity in the oxidation region, which is consistent with a
progressive deposition of layers on the Pt surface, which
in turn become less conducive to reduction.

The work of Subramanian[30] showed that phenylacetylene
could be electrochemically polymerized in DMF, so that a
layer of polyacetylene may have also formed on the electrode
in this thesis work. On the other hand, the layer could be
a series of monomers attached through the scetylenic link-
ages individually to the Pt surface. Steric considerations,
and the lability of the ($-C\equiv CH$) groups to free radical poly-
merization, suggest that the former is more likely.

The monomer solution was cycled in the CV apparatus
for one hour and the coated Pt electrode removed, and immersed
in the $.1\underline{N}$ Na_2SO_4 electrolyte to see if any layer (polymer)
was retained on the surface. Figure 31 shows that the
anodic wave didn't reappear, but it seems that the cathodic
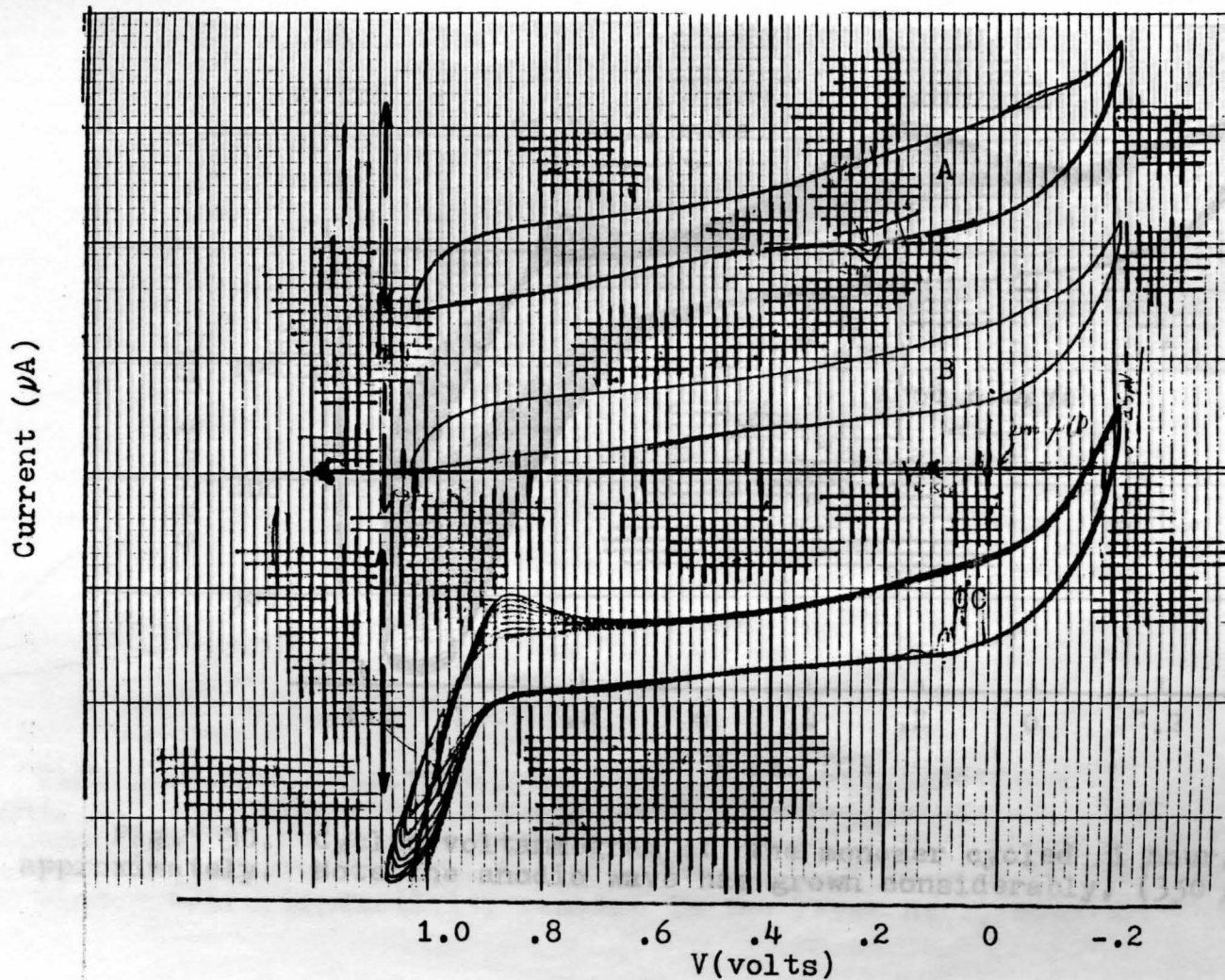
Fig. 29. Cyclic voltammogram of: (A) CAS, (B) .1$\underline{N}$ Na$_2$SO$_4$, and (C) the monomer, (CAS-O-CH$_2$C≡CH); amplitudes _increase_ each sweep.
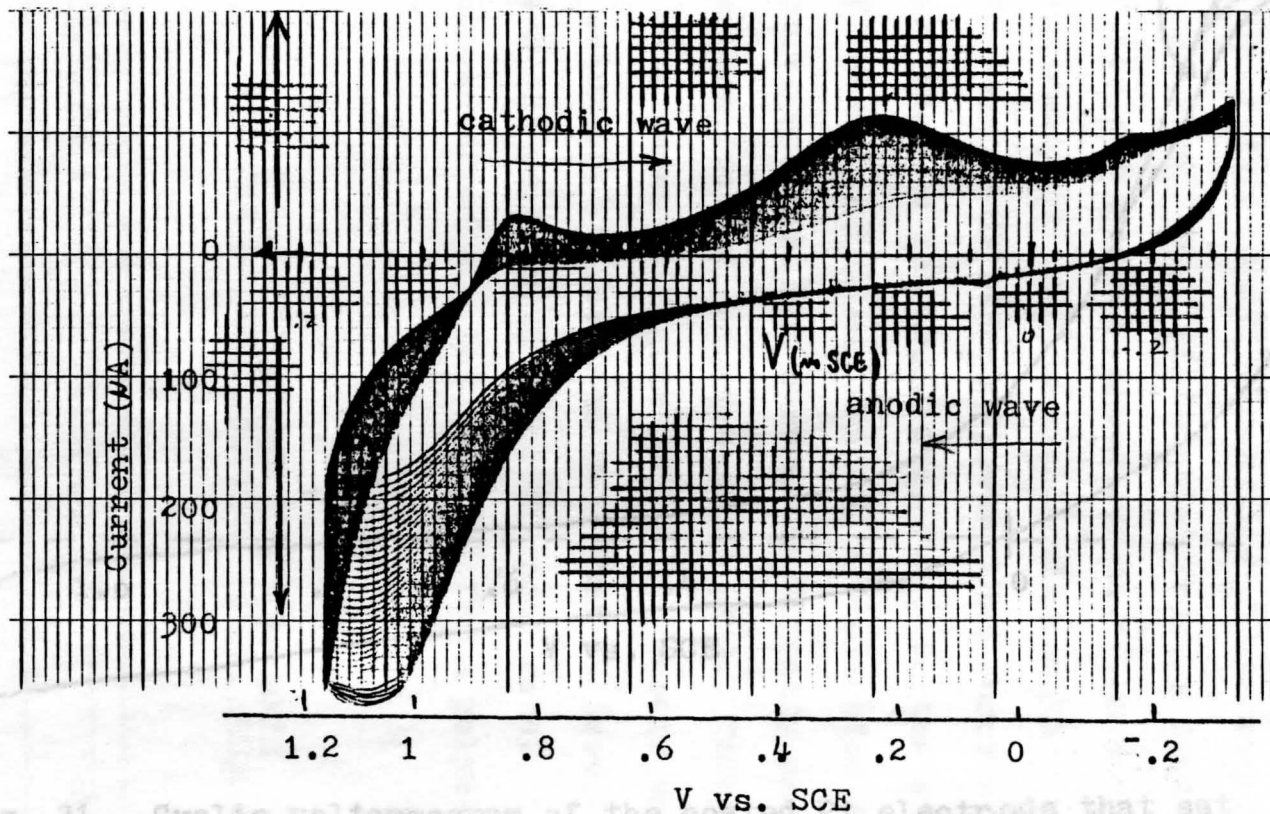
Fig. 30. Cyclic voltammogram of the monomer cycled 1 hour, approximately. Note the anodic wave has grown considerably, (350 μA).
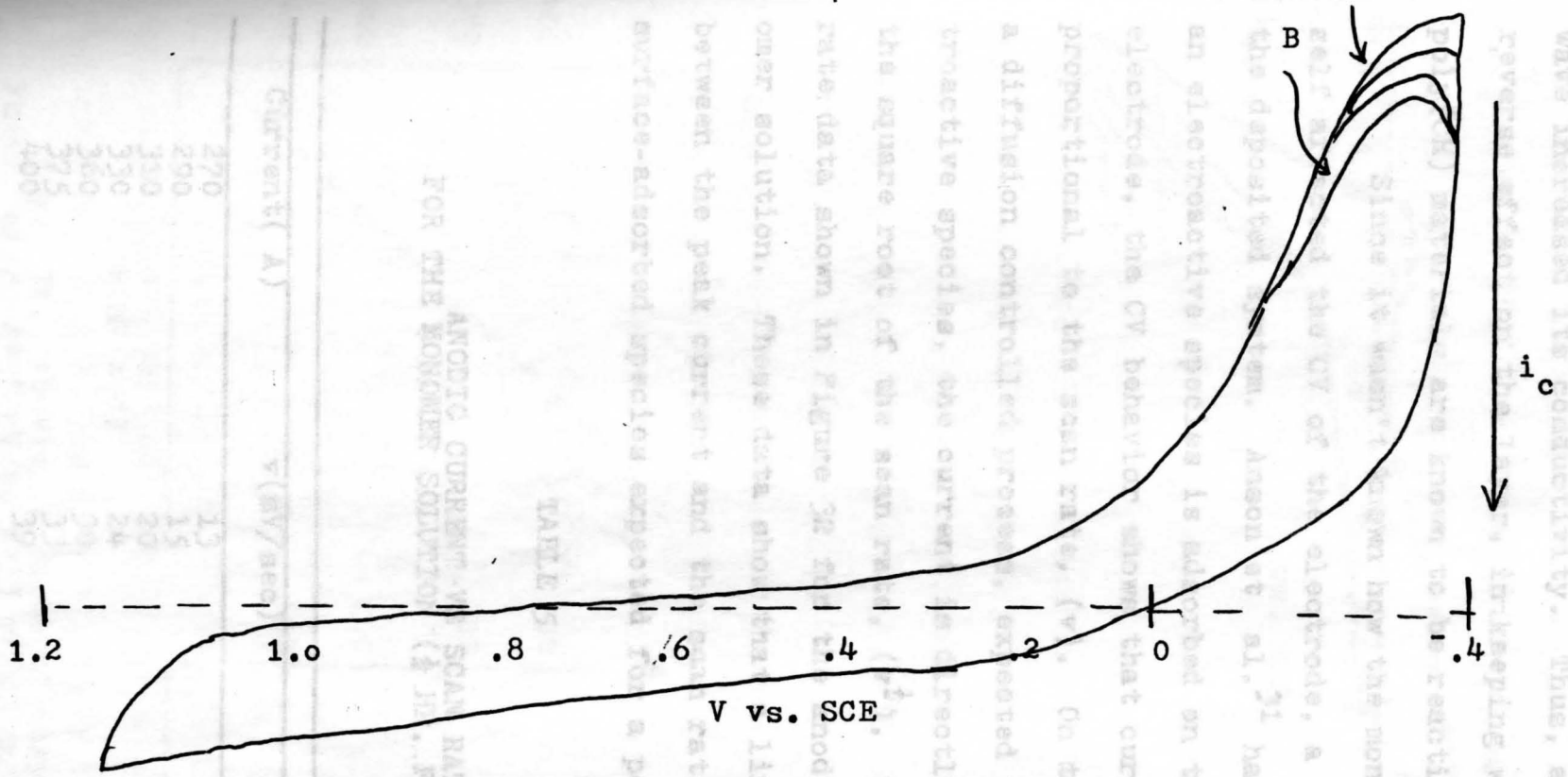
Fig. 31. Cyclic voltammogram of the coated Pt electrode that sat overnight, and was reimmersed in a .1N Na₂SO₄ the following day. There is no enhancement of the anodic wave, but the cathodic wave shows an initial increase in the cathodic current (A) and then it reverts back to the electrolyte window (B). Conductivity remains in the layer here, however.

wave increased its conductivity. Thus, air exposure had a reverse effect on the layer, in keeping with the fact that poly(CH) materials are known to be reactive with air.

Since it wasn't known how the monomer solution itself affected the CV of the electrode, a study was done on the deposited system. Anson et al.[31] have shown that if an electroactive species is adsorbed on the surface of an electrode, the CV behavior shows that current is directly proportional to the scan rate, (v). On the other hand, for a diffusion controlled process, expected for dissolved electroactive species, the current is directly proportional to the square root of the scan rate, $(v^{\frac{1}{2}})$. Table 5 lists scan rate data shown in Figure 32 for the anodic wave in monomer solution. These data show that a linearity exists between the peak current and the scan rate, indicating a surface-adsorbed species expected for a polymer layer.

TABLE 5

ANODIC CURRENT VS SCAN RATE
FOR THE MONOMER SOLUTION ($\frac{1}{2}$ HR. FILM GROWTH)

Current(A)	v(mV/sec)	$v^{\frac{1}{2}}$(mV/sec)$^{\frac{1}{2}}$
270	13	3.6
290	15	3.9
310	20	4.5
330	24	4.9
360	30	5.5
375	33	5.7
400	39	6.2

Current (A)

i_a

+1.2   1.   .6   .4   .2   0   -.2

V vs. SCE

A
B
C

Current (μA)

400
300
200
100

10   20   30   40
v(mV/sec)

Current (μA)

400
300
200
100
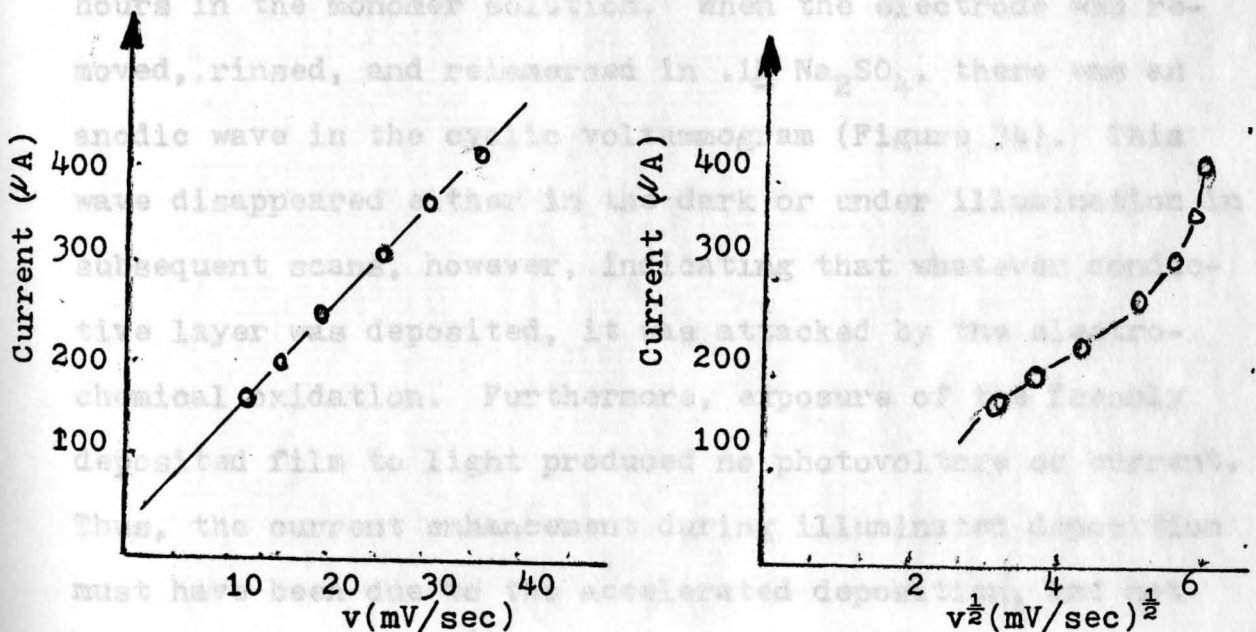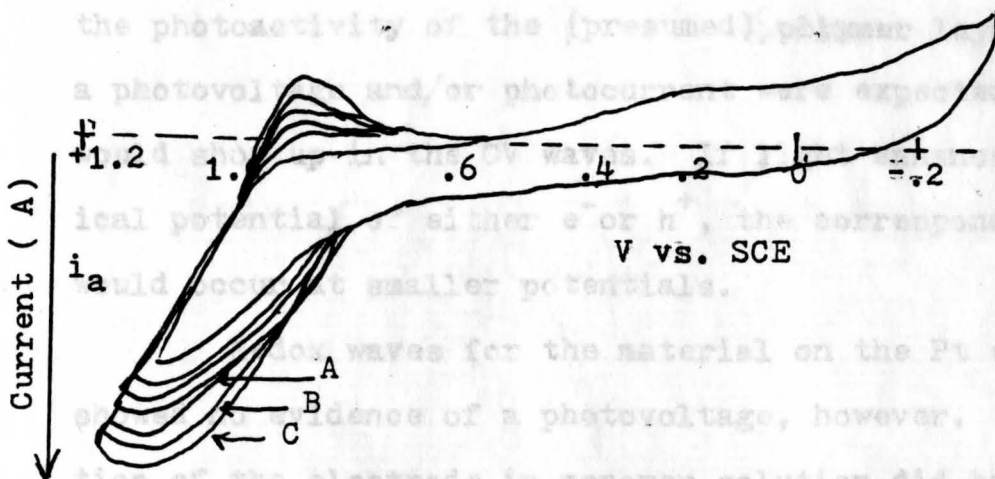
2   4   6
$v^{\frac{1}{2}}$(mV/sec)$^{\frac{1}{2}}$

Fig. 32. Above: results of varying the scan
rates, where A=33 mV/s, B=33 mV/s, and C=39 mV/s.
Below: results of plotting i_a vs. v and i_a vs. $v^{\frac{1}{2}}$.
There is linearity on the left indicating adsorption of
the electroactive species on the surface of the electrode.

A 1000W lamp, (UV and visible), was used to measure the photoactivity of the (presumed) polymer layer. Either a photovoltage and/or photocurrent were expected, which would show up in the CV waves. If light enhanced the chemical potential of either e^- or h^+, the corresponding waves would occur at smaller potentials.

Redox waves for the material on the Pt electrode showed no evidence of a photovoltage, however. Illumination of the electrode in monomer solution did have an effect on the current (Figure 33). There appeared to be either an acceleration of the deposition of the conductive layer, or an increased conductivity in the layer itself.

Lastly, the potential of the coated electrode was poised at +1.15V, where the anodic wave occurred, for two hours in the monomer solution. When the electrode was removed, rinsed, and reimmersed in .1$\underline{M}$ Na_2SO_4, there was an anodic wave in the cyclic voltammogram (Figure 34). This wave disappeared either in the dark or under illumination in subsequent scans, however, indicating that whatever conductive layer was deposited, it was attacked by the electrochemical oxidation. Furthermore, exposure of the freshly deposited film to light produced no photovoltage or current. Thus, the current enhancement during illuminated deposition must have been due to the accelerated deposition, and not the creation of e^-/h^+ pairs in the layer itself.

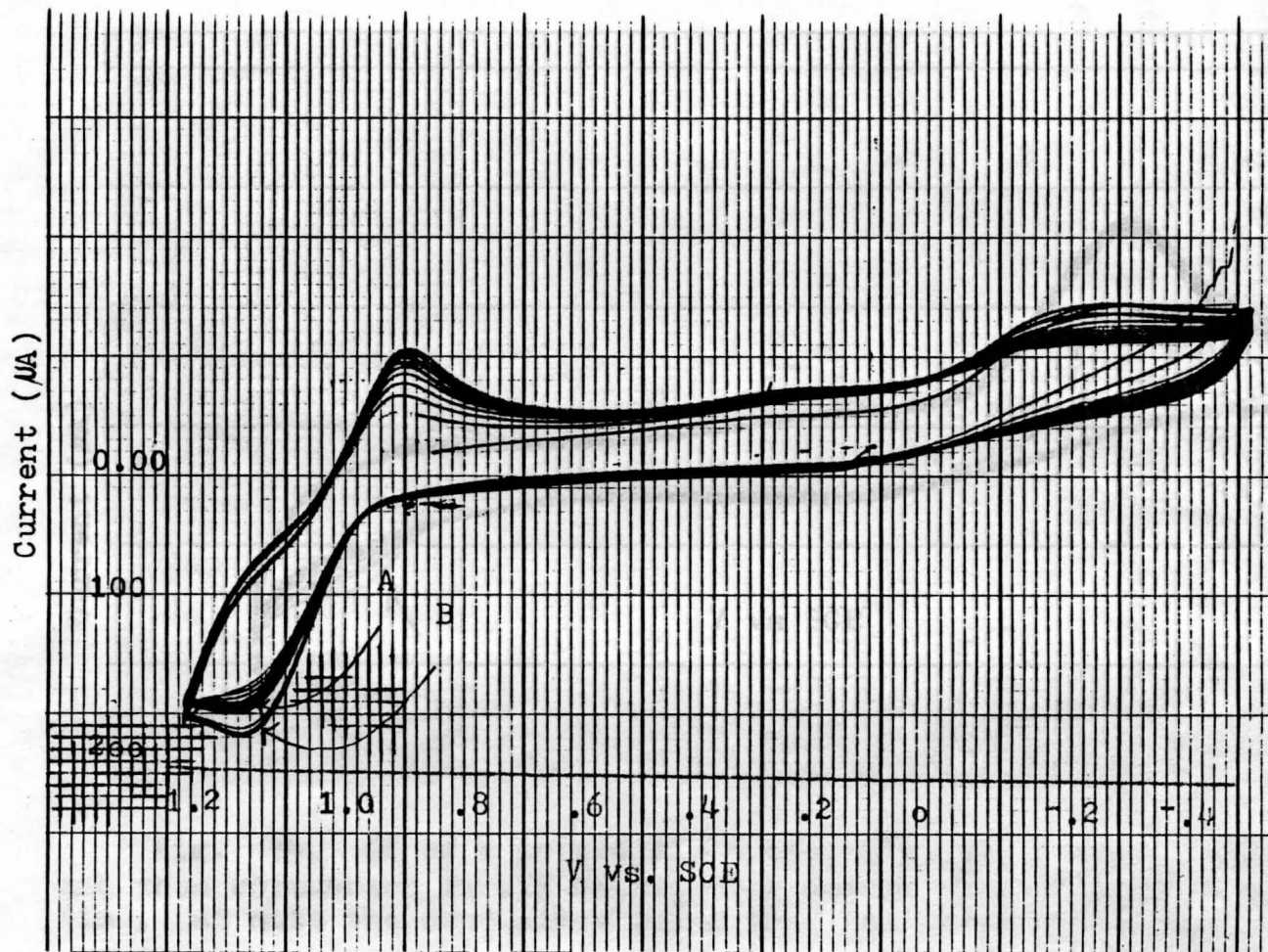The results of CV suggest there is adsorption onto the electrode surface of some partially conductive layer,

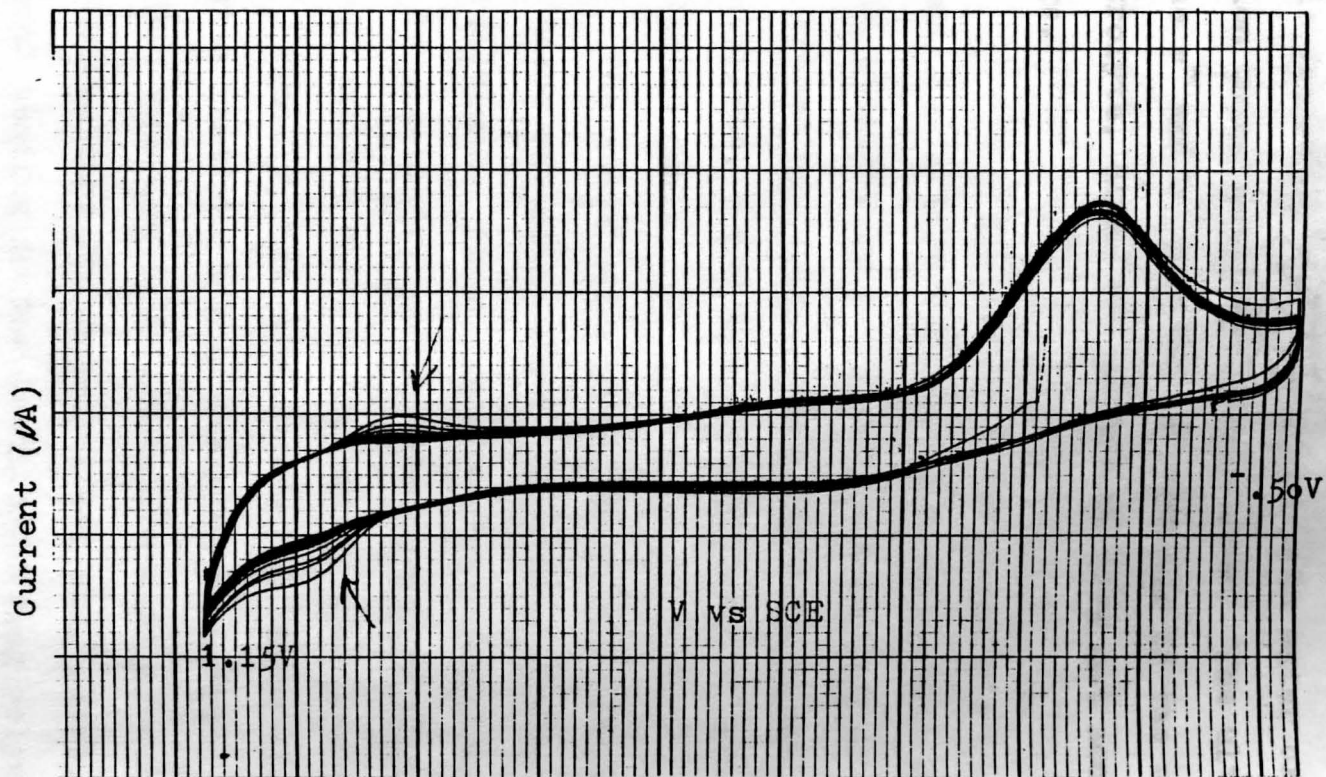Fig. 33.   CV of monomer solution in (A) Dark, (B) Illuminated

Fig. 34. CV of a poised electrode, (+1.15V, 2 hrs.), rinsed and then reimmersed in .1N Na$_2$SO$_4$. The anodic wave diminishes with time, but note the conductive layer that was there initially.

But it is not known if this layer is a poly(CH), though the
observations are consistent with this possibility. More-
over, the positions of the redox waves observed when the la-
yer is deposited are consistent with water oxidation and re-
duction being mediated by the layer. The ultimate origin
of the e^- and h^+ for the CV currents is the supporting
electrolyte, since the electrode does not accumulate trapped
charge.

The major finding of this work, that an electro-
active layer of acetylene-derived $(CH)_x$ can be electro-
deposited on a Pt surface. Since the redox waves en-
hanced by the deposition of this layer diminish with repeated
CV scan, it is inferred that the conductive structure of this
film is attacked by the redox intermediates. This, and
other reasoning, suggest that the film could well be the
polyacetylene, doped by GAS, that was originally sought as
a synthetic goal.

The redox waves noted when the film was present,
occur where one might expect the water oxidation and reduc-
tion reactions. These occur at lower voltages than for the
naked Pt electrode, so that the (probably) polymeric layer
seems to exhibit electrocatalysis (lower overvoltage).

Finally, the anodic currents under illumination
indicates that the charge carrying structure of the film is
lost when exposure to redox intermediates occur. The absence
of a photovoltage indicates either very sharp, or very lit-
tle, band bending in the (semiconducting polymer) layer.

Work should be done on obtaining more of a layer
on the Pt electrode so that evaluation of this layer can
progress. It seems that growing the conductive layer with

CHAPTER V

CONCLUSIONS

The major finding of this work is that an electro-active layer of acetylene-derivatized CAS can be electrochemically deposited on a Pt surface. Since the redox waves enhanced by the deposition of this layer diminish with repeated CV scan, it is inferred that the conductive structure of this film is attacked by the redox intermediates. This, and other reasoning, suggest that the film could well be the polyacetylene, doped by CAS, that was originally sought as a synthetic goal.

The redox waves noted when the film was present, occur where one might expect the water oxidation and reduction reactions. These occur at lower voltages than for the naked Pt electrode, so that the (problably) polymeric layer seems to exhibit electrocatalysis (lower overvoltage).

Finally, the anodic currents under illumination indicates that the charge carrying structure of the film is lost when exposure to redox intermediates occur. The absence of a photovoltage indicates either very sharp, or very little, band bending in the (semiconducting polymer) layer.

Work should be done on obtaining more of a layer on the Pt electrode so that evaluation of this layer can progress. It seems that growing the conductive layer with

repeated cycling produces different kinds of films than
a fixed electropolymerization.

If band bending isn't observed through photovol-
tages, the separation of the e^-/h^+ isn't attained. From
the following equation:

$$w = (2\mathcal{E}\mathcal{E}_0 V_b/qN)^{\frac{1}{2}} \tag{6}$$

where V_b is the amount of band bending in the depletion
layer, N is the charge carrier density in the semicon-
ductor, q is the electronic charge, $\mathcal{E}$ is the dielectric
constant of the semiconductor, $\mathcal{E}_0$ is the permittivity
of free space, and w is the width of the depletion layer.
The width of the depletion layer can be changed by varying
the charge carriers, N, which is presumed to be the dye
carrier density. This can be achieved by copolymerizing
propargyl alcohol with the CAS monomer already synthesized.
In semiconductors, w varies from $100°A$ to a few microns,
and in metals, the space charge region is infinitesimally
small, which is why charges induced at the electrode are
maintained at the surface. [32]

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