

ABSTRACT

PHOTOELECTROCHEMISTRY WITH POLYMER ELECTRODES:

YOUNGSTOWN STATE UNIVERSITY

POLY(PRIMULIN- AND TOLUIDINE BLUE-O)ACETYLENE

Graduate School

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Poly(Primulin and Toluidine Blue-O)Acetylene"

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ABSTRACT

and oxygen. By using both cationic and anionic dyes, n- and p-type PHOTOELECTROCHEMISTRY WITH POLYMER ELECTRODES: photochemical POLY(PRIMULIN- AND TOLUIDINE BLUE-O)ACETYLENE polymer electrolyte cells, when photochemically illuminated and electrically connected, may in principle photocatalyze the decomposition of water.

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The objectives of this research are twofold : the synthesis of two polyacetylene-ionic dye polymers and subsequent experimentation on their semiconductive and photoelectric properties.

The synthetic approach of chemically coupling a poly(acetylene) backbone (the conducting portion of the molecule) to the light absorbing moiety (the organic-ionic dye), has not, until now, been experimentally shown.

The chemical route was to couple an acetylene-carboxylic acid with an amine function on the ionic dye forming an amide linkage. Verification of the presence of both the amide linkage and the polymerization of the triple bond came primarily from infrared and nuclear magnetic resonance spectroscopy.

The semiconductive properties of these polymers were tested utilizing cyclic voltammetry. Photoconduction was ascertained by the same process using also a 1000 watt ultraviolet source for photoexcitation of the polymer. One potential use of this system is to split water into hydrogen

ACKNOWLEDGEMENTS

and oxygen. By using both cationic and anionic dyes, n- and p-type semiconducting polymers were prepared. As photochemical diode materials, these polymers, when simultaneously illuminated and ohmically connected, may in principle photocatalyze the decomposition of water.

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Dr.Mettee, Mom and Dad: Thank you so very much.

Dr.Mincey and Dr.Schildcrout-thank you for your time spent
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It is intended that this n- or p-type dye polycetylene will mimic

CHAPTER I

INTRODUCTION

The search for inexpensive and stable materials which will both absorb the sun's radiant energy and separate water into hydrogen (H_2) and oxygen (O_2) has been limited primarily to inorganic semiconductors and surface derivatized silicon. Our polymeric photoelectrodes offer a flexibility in the design of the light absorbing and charge separating properties required by such units, which is not currently possible.

We decided to design an organic semiconductor even though many inorganic and silicon derivatized units already exist because the use of polymer semiconductor electrodes to photocatalyze the decomposition of water with natural sunlight is useful as most inorganic materials absorb only ultraviolet radiation. The solar production of hydrogen as a fuel is an important alternative energy source for the near future as the existing fossil fuels are rapidly approaching depletion.

Therefore, several synthetic routes were designed to couple acetylene (the polymerization agent) to organic dyes (the light absorbers), which contain anionic and cationic subgroups, to produce the starting monomers. These charged subgroups are necessary to produce an electrical gradient which separates charge, producing chemical potential, when light

is absorbed. (e^-/h^+) species generated are detected by the electrochem. It is intended that this "n- or p-type dye"- process polyacetylene will mimic an ordinary n- or p-type semiconductor in the following manner: When an n-type semiconductor is immersed in an electrolyte solution, the majority current carriers (electrons) leave the surface of the semiconductor and enter the solution so as to balance the Fermi levels of both. This effect creates a "depletion layer" at the surface of the semiconductor where light is absorbed. This depletion layer is a barrier against the further loss of electrons, and is reflected by "bending" the valence and conduction bands near the surface. This forms the charge gradient in which electron/hole pairs generated by the band gap or greater illumination are separated (see figure 1), leading to the observed photoelectrochemistry.

In the n-type dye polyacetylene version, a covalently bonded quaternary nitrogen atom is counterbalanced by a negatively charged chloride ion. When immersed in water, the loss of Cl^- from the dye moiety forms a charge gradient, which will separate the (e^-/h^+) pairs created by the absorption of light corresponding to the band separation characteristic of the dye.

Analogously, in the 'p-dye' polyacetylene, a covalently bound SO_3^- group has a sodium counter ion. When immersed in water the loss of Na^+ forms a charge gradient which will segregate the (e^-/h^+) pairs created by light absorption corresponding to the band gap characteristic of the dye.

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The (e^-/h^+) species generated are detected by the electrochemical technique of voltammetry. The specific process used was cyclic voltammetry. Briefly, voltammetry is an electrochemical technique in which the current at an electrode is measured as a function of the potential, or voltage, applied to that electrode. The potential is varied in a systematic manner, and the resulting current-voltage plot is called a voltammogram. The most common application of voltammetry is for analytical purposes and for the characterization of electrode surface processes.

Once establishing the electroactivity of these polymers, the final objective was to determine if they were also photoactive and, if so, able to split water. This was done by using the same basic setup of the voltammetry experiment only now utilizing a high power UV-visible light source in addition to the applied potential.

Assuming that both n-type and p-type polymers were available, what thermodynamic requirements must be met in order to achieve the splitting of water? The elementary conditions are that the valence band of the n-type material must be at a more positive redox potential than the H_2O/O_2 couple, while the conduction band of the p-type must be at a more negative redox potential than the H^+/H_2 couple. Band bending (V_b) is calculated here from the flat band potential (V_{fb}), the redox potential (V_R) of the H_2O/O_2 couple at the anode, and the H^+/H_2 at the cathode, ($V_b = V_R - V_{fb}$). The Fermi level for the combined system lies between these two

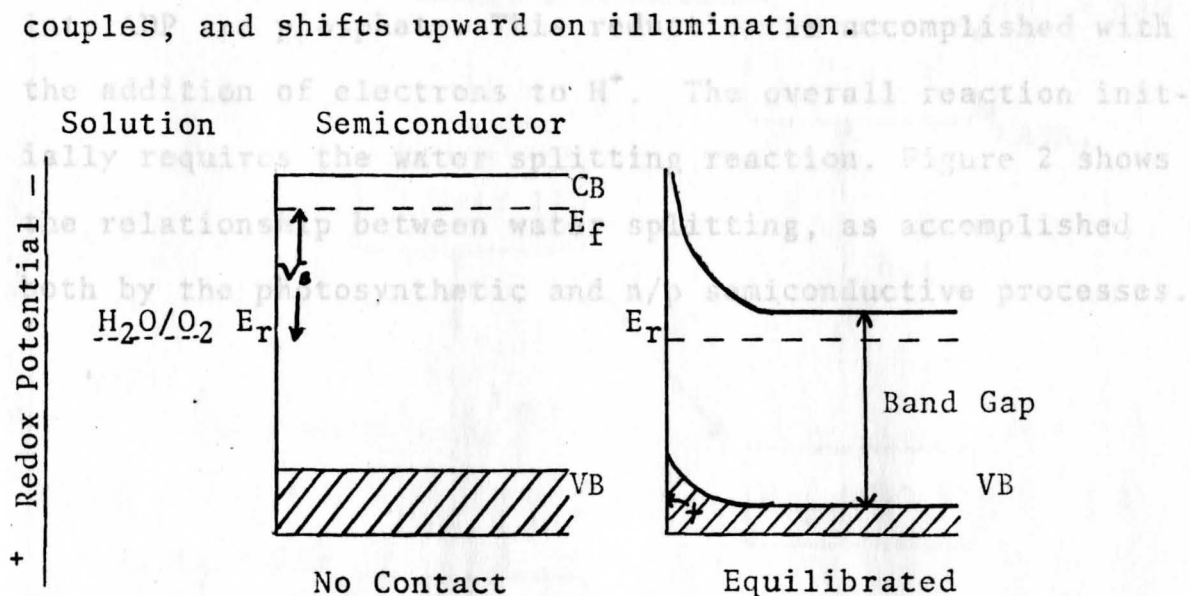


Figure 1. Semiconductor band bending and charge separation after the absorption of light in an n-type oxidizing semiconductor.

Plants perform these processes using biological macromolecules of chlorophyll. In photosynthesis, two basic mechanisms are at work, called the light and dark reactions. The light reaction achieves the splitting of water. This involves the capture of light energy by light absorbing pigments and its conversion into the chemical energy of ATP and certain reducing agents, namely NADPH. In this process hydrogen atoms are removed from water molecules and used to reduce $NADP^+$. Molecular oxygen (O_2) forms on the opposite side of the membrane, where water is oxidized. Simultaneously, ADP is phosphorylated to ATP. The dark reaction takes the energy rich products of the first phase, NADPH and ATP, and utilizes them as energy sources to bring about the reduction of carbon dioxide to yield glucose; simultaneously, NADPH is **oxidized** to $NADP^+$, and the ATP is broken down again

Photosystems I & II

into ADP and phosphate. This reduction is accomplished with the addition of electrons to H⁺. The overall reaction initially requires the water splitting reaction. Figure 2 shows the relationship between water splitting, as accomplished both by the photosynthetic and n/p semiconductive processes.

Reduction Potential

Reduction Potential

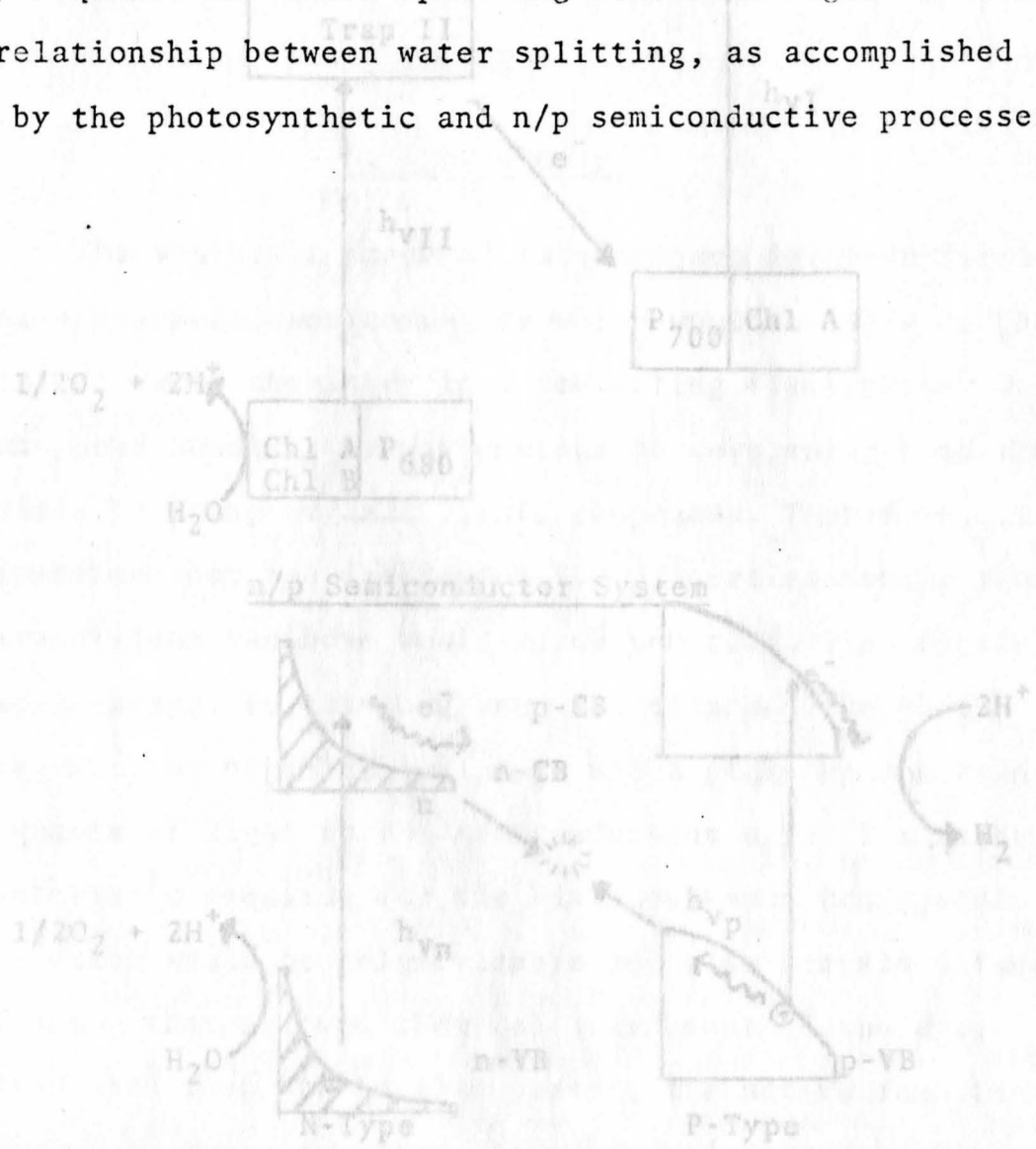


Figure 2. The light absorbing and charge separating functions of natural photosystems I and II, in addition to the water redox reactions, are artificially duplicated by p- and n-type semiconductors. (6)

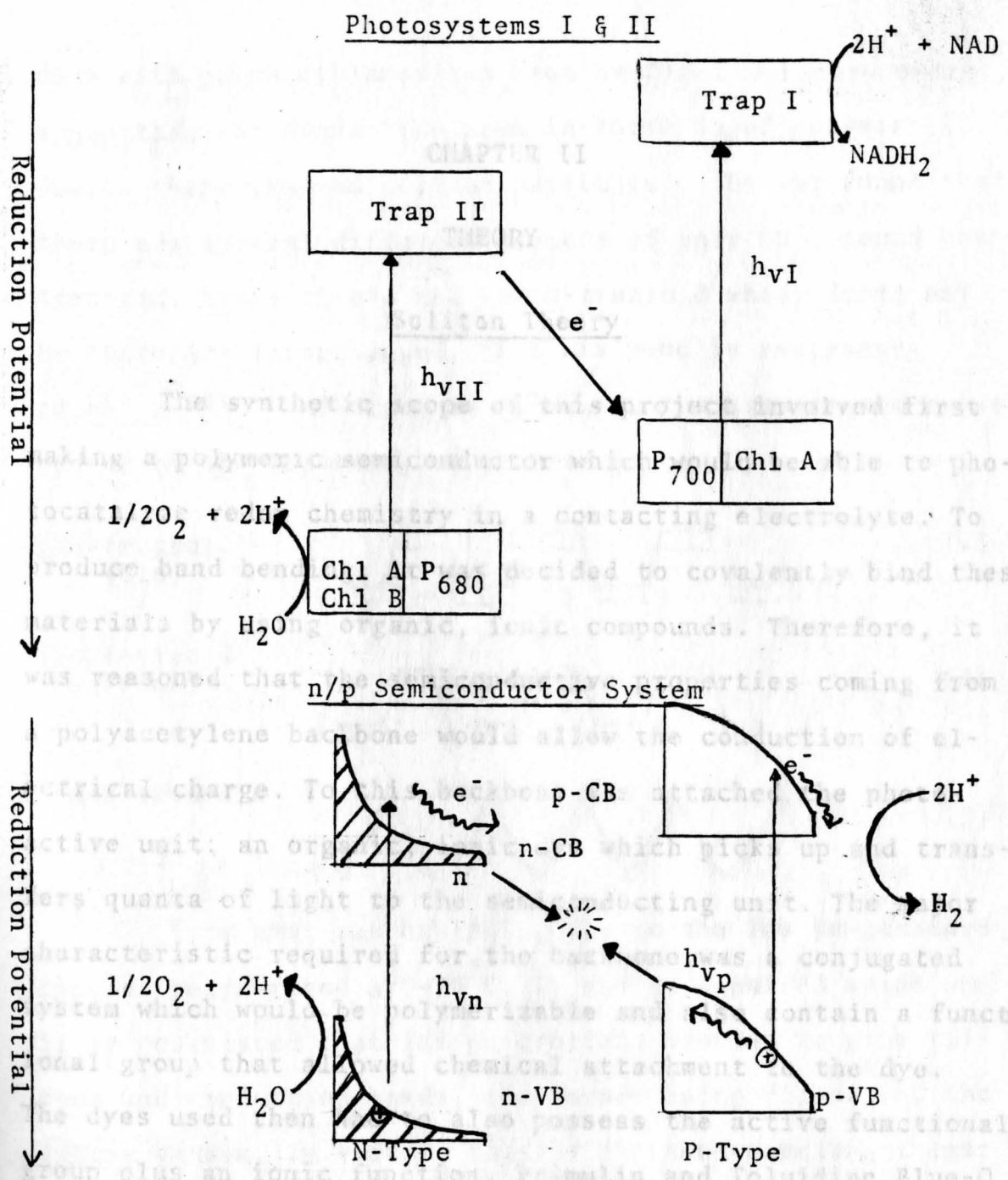


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CHAPTER II

due to these charged soliton particles. He has found that

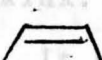
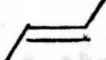
THEORY

there are several different isomers of poly(CH) named cis-transoid, trans-cisoid and trans-transoid whose forms may be thermally interchanged. If a cis bond is represent-

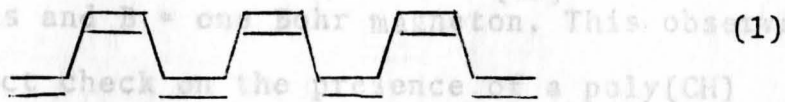
Soliton Theory

The synthetic scope of this project involved first making a polymeric semiconductor which would be able to photocatalyze redox chemistry in a contacting electrolyte. To produce band bending, it was decided to covalently bind these materials by using organic, ionic compounds. Therefore, it was reasoned that the semiconductive properties coming from a polyacetylene backbone would allow the conduction of electrical charge. To this backbone was attached the photoactive unit: an organic, ionic dye which picks up and transfers quanta of light to the semiconducting unit. The major characteristic required for the backbone was a conjugated system which would be polymerizable and also contain a functional group that allowed chemical attachment to the dye. The dyes used then had to also possess the active functional group plus an ionic function. Primulin and Toluidine Blue-O were chosen as the dyes and propiolic acid as the polymerizing agent.

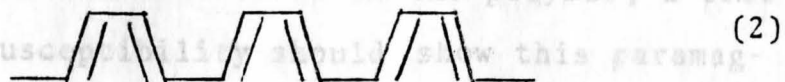
The trans polyacetylene chain is a semiconducting backbone, as it is one of the simplest organic metals which has unpaired spins. These unpaired electrons are given the name "solitons" by physicists. Much of the work having been

done with polyacetylenes has been by Chien and co-workers⁽⁸⁾, suggesting the conduction seen in these doped polymers is due to these charged soliton particles. He has found that there are several different isomers of poly(CH), named cis-transoid, trans-cisoid and trans-transoid whose forms may be thermally interchanged. If a cis bond is represented as  and trans as , the isomers are represented by the following structures.

Cis-transoid
(Cis)



Trans-cisoid
(Trans)

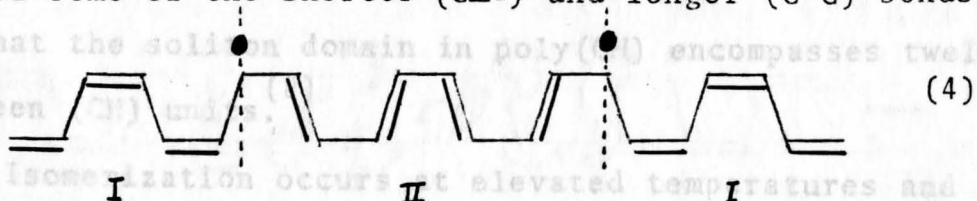


Trans-transoid



Type one, the cis-poly(CH), is the low temperature species polymerized at -70°C . It has no unpaired spins and it is postulated that its pi orbitals overlap to give valence and conduction bands, the former being filled and the latter vacant. In effect, this is the nonconducting isomer.

It was proposed that the second, trans, isomer results from the isomerization of a portion of the backbone from type one to type two by a low energy process of interchange of some of the shorter (C=C) and longer (C-C) bonds:



The black dots represent the unpaired spins or solitons which are not localized on a single carbon atom. On each side of the neutral soliton there is a phase change of the pi wave function. The amplitude vanishes at the center of the soliton domain and this region is then called the pi phase kink.

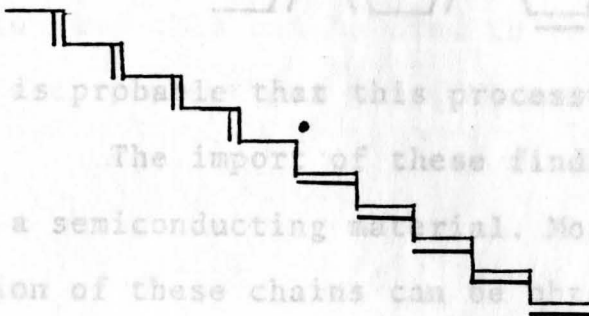
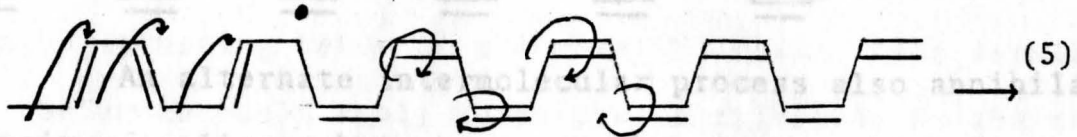
It was also found that the solitons are paramagnetic and obey the Curie dependence of $N_s B^2 / kT$ where N_s = the number of solitons and B = one Bohr magneton. This observation allows a direct check on the presence of a poly(CH) chain. Therefore, if solitons exist in the polymer, a test of its magnetic susceptibility should show this paramagnetism.

Chien also found that the cis-poly(CH) was only cis rich; it has varying amounts of isomerized structures depending on the handling of the sample. Moreover, the thermally dependent equilibria between the isomers controls the concentration of the solitons.

The width of the soliton domain or its extent of delocalization was clarified by electron paramagnetic resonance studies. Specifically, the greater the delocalization then the smaller the wave function amplitude becomes, and it is this relation which narrows the epr line width, which is then the measured variable. Using this fact, it was determined that the soliton domain in poly(CH) encompasses twelve to sixteen (CH) units.⁽⁸⁾

Isomerization occurs at elevated temperatures and at

($T=145^{\circ}\text{C}$) bond rotation occurs and thermodynamically stable trans isomers are formed:



The solitons are very mobile at room temperature and their mobility decreases with a concurrent temperature decrease. Another phenomenon of these species is that they are not spatially fixed; they can migrate and change structure which can result in the degradative process of annihilation:



Other work clarifies the solitons as a moving domain wall or excitations which migrate along the short and long alternating bonds of the poly(CH) chain. Also detailed

An alternate intermolecular process also annihilates a pair of solitons but preserves the pi phase kink (cross-linking). This effect is explained as the electronic structure of the soliton exhibits a localized state

2 the pi phase kink. While this localized state is spin unpaired,

the distorted valence band continues to have a spin equal to zero. Therefore the neutral soliton has a spin equal to 1/2. Susceptibility therefore contains a Curie-law contribution and this can be used to count the number of soliton

It is probable that this process occurs during heating.

The import of these findings is that poly(CH) can be a semiconducting material. Moreover, proof for the formation of these chains can be obtained by magnetic susceptibility measurements. Also, there is no reason to suspect that these molecular isomerization and annihilation processes would not occur with substituted poly(CH) chains. It is concluded that these mobile charge carriers provide a mode of charge transport along the conjugated chain.

Heeger et.al. have used nuclear magnetic resonance⁽²³⁾ to demonstrate the existence of mobile solitons in poly(CH). Their spectra have demonstrated one-dimensional electron spin diffusion in the polymer, both doped and undoped. This effect is manifested primarily by a large peak broadening of the alkene absorption region.

Other work clarifies the solitons as a moving domain wall, or excitations, which migrate along the short and long alternating bonds of the poly(CH) chain. Also detailed is the anomalously small Curie-law contribution to the magnetic susceptibility. This effect is explained as the electronic structure of the soliton exhibits a localized state at the center of the wall, containing one e^- for the neutral pi phase kink. While this localized state is spin unpaired, the distorted valence band continues to have a spin equal to zero. Therefore the neutral soliton has a spin equal to $\frac{1}{2}$. Susceptibility therefore will contain a Curie-law contribution and this can be used to count the number of soliton defects present per poly(CH) chain.

The electrical conductivity of crystals depends on the magnitude of the band gap (ϵ) between the filled valence band and the empty, higher energy conduction band. The ratio of the number of e^- thermally excited to the conduction band to the number in the valence band is given by a Boltzmann factor $e^{-\epsilon/2kT}$. When an e^- in an intrinsic semiconductor jumps into the conduction band it leaves behind a hole in the valence band. The e^- in a completely filled valence band could make no contribution to the conductivity. As soon as holes appear, however, the remaining e^- find some empty states available, and can then contribute to the conductivity. A hole in a band of negative e^- is effectively a point of positive charge. The jump of an e^- into a hole is equivalent to the jump of a positive charge into the position vacated by the e^- . Therefore the motion of e^- in an almost filled valence band behaves as if the holes were positive charges moving in an almost empty hole band.

When a phosphorous atom is substituted for a silicon (Si) atom, in a pure Si crystal, four of the

Semiconductor Theory

A brief definition of a semiconductor is given here in order to clarify the working mechanism of these organic semiconductors. There are three kinds of semiconductor devices known as intrinsic, n- and p-types. An intrinsic semiconductor is pure (undoped), whereas n- and p-types are doped with other materials in order to produce particular semiconducting properties.

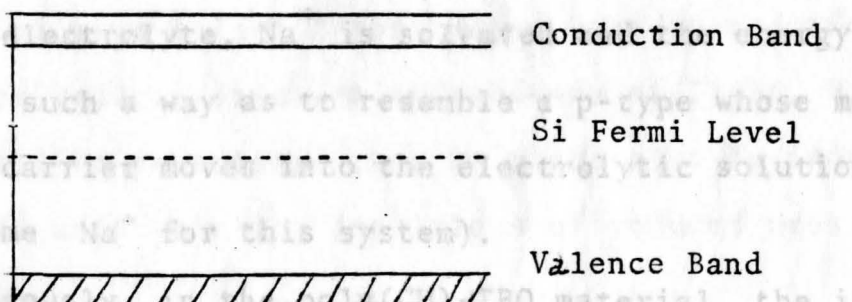
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When a phosphorous atom is substituted for a silicon (Si) atom, in a pure Si crystal, four of the

valence e^- of P can enter the valence band, but the fifth e^- must enter some level of higher energy. This energy state is only 0.012eV below the Si conduction band. Therefore, the fifth e^- in the donor levels can easily be thermally excited into the conduction band. The doped semiconductor will have a greatly enhanced conductivity compared with the pure intrinsic semiconductor. Such a material is termed an n-type, because the majority carriers of current are negatively charged e^- . A dopant which can supply e^- to the conduction band is termed a donor and the extra energy levels just below the conduction band are called donor levels.

If the dopant has fewer valence electrons than the conductor atom, there holes, or missing e^- , in the valence band. Consequently, a new level occurs in the valence band. In the case of boron(B) in Si, these donor levels are only 0.01eV above the top of the valence band. Electrons can readily jump from the top of the valence band to fill such acceptor levels. The positive holes left in the valence band strongly enhance the electrical conductivity and the Si(B) doped material becomes a p-type semiconductor. The following figures illustrate these semiconductor types:

Intrinsic Semiconductor (Si)



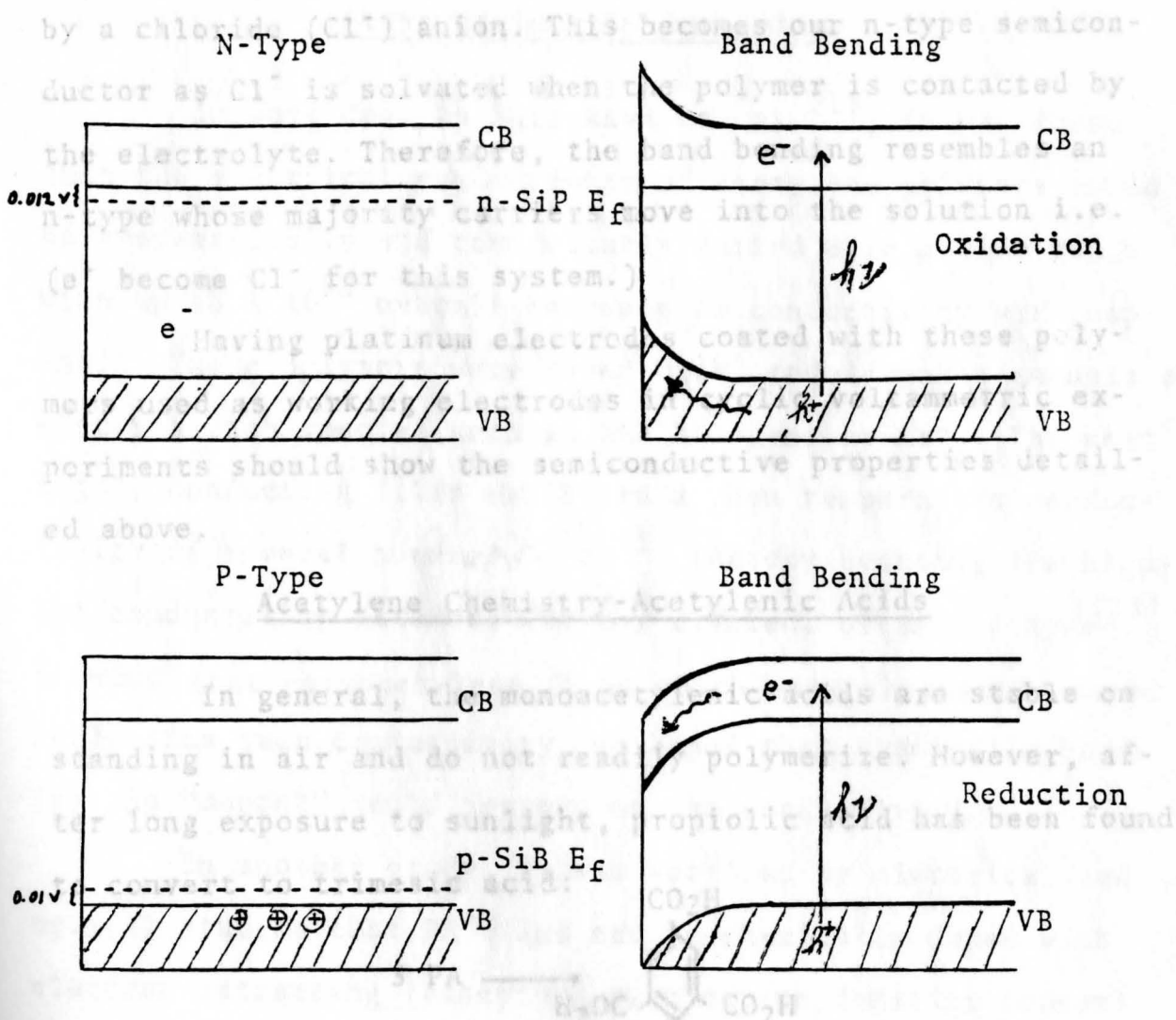


Figure 3 : Semiconductor types with dopant, showing also typical band bending.

In the poly(CH)-PR material, the ionic function on the dye is a sulfonic acid (SO_3^-) anion counterbalanced by a sodium (Na^+) cation. This, then, is the organic counterpart of a p-type semiconductor, as when the polymer is contacted by an electrolyte, Na^+ is solvated and the energy bands bend in such a way as to resemble a p-type whose majority charge carrier moves into the electrolytic solution (i.e. h^+ become Na^+ for this system).

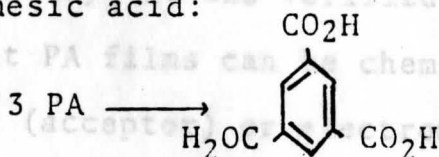
Analogously, in the poly(CH)-TBO material, the ionic dye function is a quaternary nitrogen (N^+) atom balanced

by a chloride (Cl^-) anion. This becomes our n-type semiconductor as Cl^- is solvated when the polymer is contacted by the electrolyte. Therefore, the band bending resembles an n-type whose majority carriers move into the solution i.e. (e^- become Cl^- for this system.)

Having platinum electrodes coated with these polymers used as working electrodes in cyclic voltammetric experiments should show the semiconductive properties detailed above.

Acetylene Chemistry-Acetylenic Acids

In general, the monoacetylenic acids are stable on standing in air and do not readily polymerize. However, after long exposure to sunlight, propiolic acid has been found to convert to trimesic acid:



Accordingly, the PA sample was stored under dark, cool conditions.

Vinyl propiolic acid ($\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$) is reported to polymerize on heating in vacuum to give a rubber like yellow substance; and the isomeric acid ($\text{CH}\equiv\text{C}-\text{CH}=\text{CH}-\text{CO}_2\text{H}$) is known to undergo self-polymerization rapidly under the conditions of reduced pressure and absence of light. From this, it could be postulated that PA might also be induced to polymerize under similar conditions of reduced pressure and heating.

It was concluded that in considering possible poly-

acetylene deriva Polyacetylene Conductivity or all of the hv-

In work done by Shirakawa et. al.⁽¹³⁾, it was found that the electrical conductivity of acetylene polymers could be systematically and controllably varied over a wide range with up to a 10^{11} overall increase in conductivity with doping. These polymers were doped with predetermined amounts of electron rich species, such as the halogens or AsF_5 . The most highly conducting films exhibited a room temperature conductivity of several hundred $\Omega^{-1}cm^{-1}$, thereby becoming the highest conductivity observed for any covalent organic polymer.⁽¹³⁾ Knowing that polyacetylene films which were physically doped could show such conductivity, we hoped that chemically bonding the "dopant" would improve on the conductivity.

In another study, it was verified by electrical and optical studies that PA films can be chemically doped with electron-attracting (acceptor) or electron donating (donor) species in a manner analogous to that found for simple classical semiconductors such as silicon. The conductivity was found to progressively increase with increasing amount of dopant. With certain dopants a semiconductor-metal transition occurs at a few mole percent of dopant concentration to give flexible films of organic metals having a very high room temperature conductivity. Extrapolating this observation to our systems indicated that if just one or two dye molecules per polymer chain (12-16 CH's) could be bonded, then we would have a working semiconductor.

It was concluded that in considering possible poly-

acetylene derivatives, replacement of some or all of the hydrogen atoms in $(-CH-)_x$ with organic groups should lead to the development of a large new class of conducting organic polymers with the electrical properties of a semiconductor. ⁽¹³⁾

The proposed substitution of at least several $-(CH)-$ hydrogen atoms with a dye molecule, thus, is a step in this direction. One target of this research project was the synthesis of an acetylene-ionic dye linked polymer. Several routes were available for this synthesis including an amide linkage, phenolic ester coupling and nonhydrolyzable ether bonds. This work is primarily concerned with the amide coupling scheme.

Having chosen an acetylene backbone for the proposed polymer, propiolic acid (PA) was purchased from the Farchan chemical company. The dye materials used were Toluidine Blue-O (TBO) and Primulin (PR), purchased from Aldrich chemicals. TBO is a cationic, n-type, oxidizing dye, its specific qualities include primary amine coupling, absence of azo functions, a tetraalkylated nitrogen (N^+) and an oxidizable sulfur atom. In turn, PR is an anionic, p-type, reducing dye which also has primary amine coupling, no azo or quinone functions and a strong acid anion.

The chemical materials employed and their structural representations are given by the following structures:



CHAPTER III

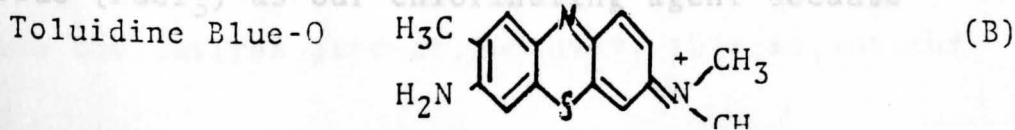
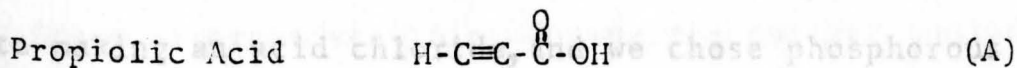
EXPERIMENTAL

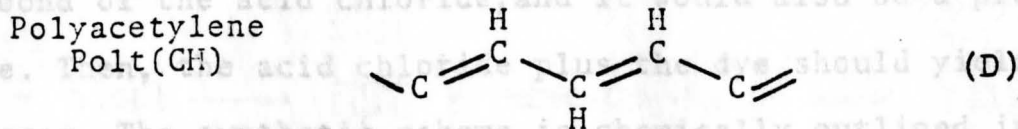
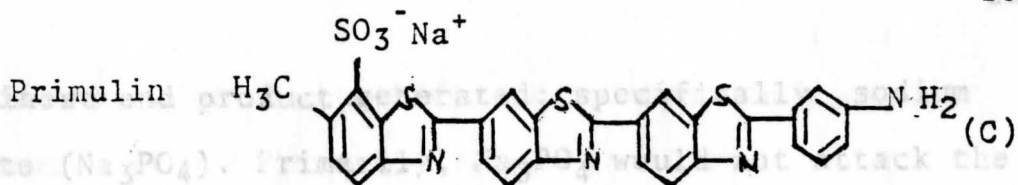
Monomer Formation

One target of this research project was the synthesis of an acetylene-ionic dye linked polymer. Several routes were available for this synthesis including an amide linkage, phenolic ester coupling and nonhydrolyzable ether bonds. This work is primarily concerned with the amide coupling scheme.

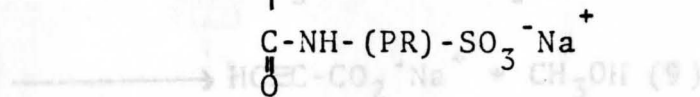
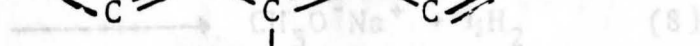
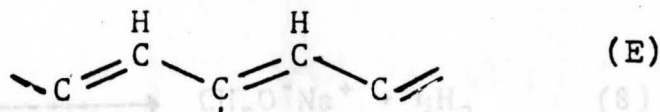
Having chosen an acetylene backbone for the proposed polymer, propiolic acid (PA) was purchased from the Farchan chemical company. The dye materials used were Toluidine Blue-O (TBO) and Primulin (PR), purchased from Aldrich chemicals. TBO is a cationic, n-type, oxidizing dye, its specific qualities include primary amine coupling, absence of azo functions, a tetraalkylated nitrogen (N^+) and an oxidizable sulfur atom. In turn, PR is an anionic, p-type, reducing dye which also has primary amine coupling, no azo or quinone functions and a strong acid anion.

The chemical materials employed and their structural representations are given by the following structures:

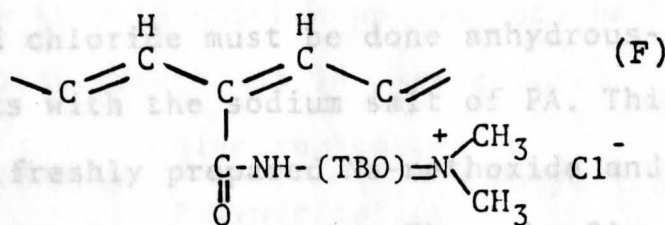




Poly(CH)-PR



Poly(CH)-TBO



The formation of the acid chloride must be done anhydrously, and conveniently starts with the sodium salt of PA. This was done by adding PA to freshly prepared sodium hydroxide and isolating and drying the resultant crystals. Then the PA-Na salt was introduced into the POCl_3 with acid chloride and Na_3PO_4 being formed as products.

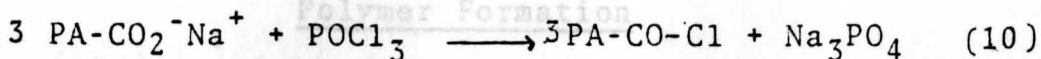
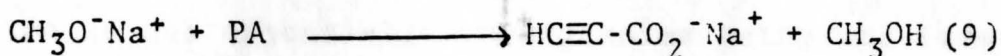
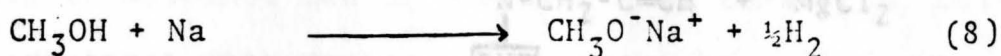
Having isolated the PA-Cl, it is then reacted with the two dyes to form the monomer:

Monomer Synthesis/Acid Chloride Route

$\text{HO}-\text{C}(=\text{O})-\text{CO}-\text{Cl} + \text{H}_2\text{N}-(\text{TBO})-\text{N}^+(\text{CH}_3)_3 \longrightarrow \text{HO}-\text{C}(=\text{O})-\text{CO}-\text{NH}-(\text{TBO})-\text{N}^+(\text{CH}_3)_3$

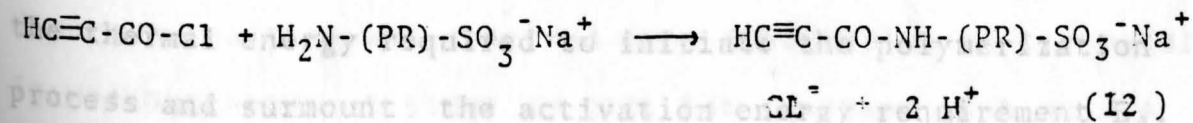
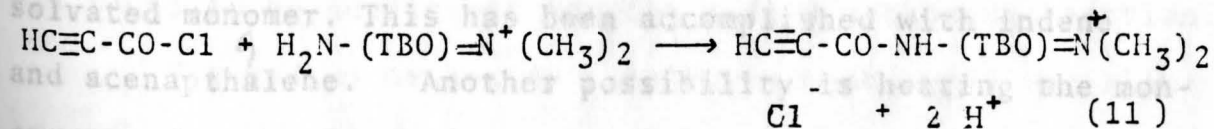
What we wanted to do, then, was form an amide linkage $-(\text{NH}-\text{CO})-$ between the dyes and the acid. A reasonable way to do this is form the highly reactive acid chloride, and then react it with an amine. There are several synthetic routes to making an acid chloride, and we chose phosphorous oxychloride (POCl_3) as our chlorinating agent because will give the desired product, however, this is not the

of the inert end product generated: specifically sodium phosphate (Na_3PO_4). Primarily, Na_3PO_4 would not attack the triple bond of the acid chloride, and it would also be a precipitate. Then, the acid chloride plus the dye should yield the monomer. The synthetic scheme is chemically outlined in the following equations:



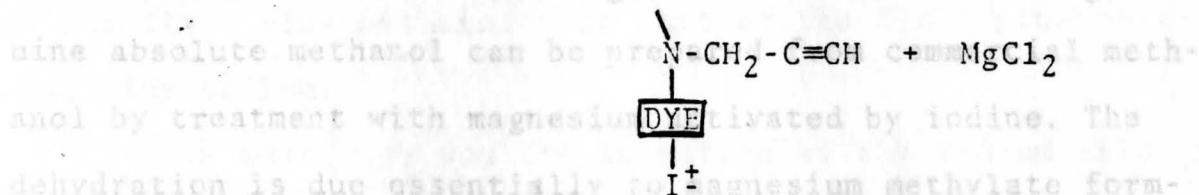
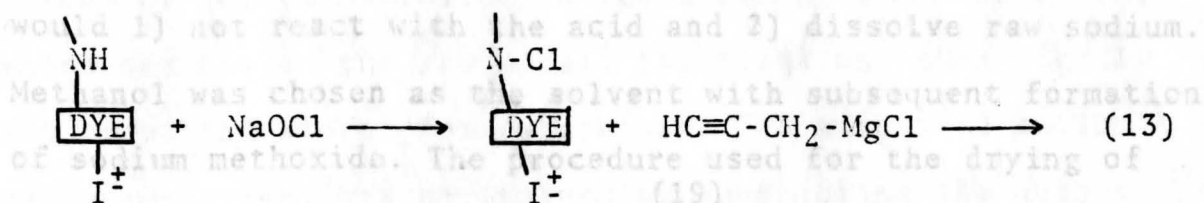
The formation of the acid chloride must be done anhydrously, and conveniently starts with the sodium salt of PA. This was done by adding PA to freshly prepared Na-methoxide and isolating and drying the resultant crystals. Then the PA-Na salt was introduced into the POCl_3 with acid chloride and Na_3PO_4 being formed as products.

Having isolated the PA-Cl, it is then reacted with the two dyes to form the monomer:



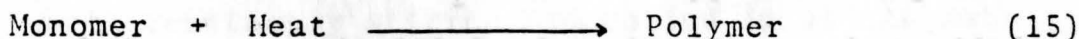
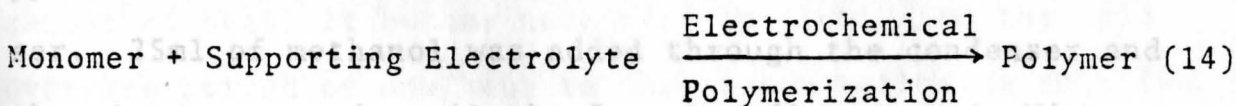
Other alternatives to producing the monomer include the alkylation of amines using a Grignard reagent which will give the desired product, however, this is not the

method of choice as it is difficult to separate and purify the monomer.



Polymer Formation

About 1.25g of dry magnesium turnings and .125g of resublimed iodine were placed in a 500ml round bottomed pyrex flask and fitted with a double surface reflux condenser.



If the monomeric material can be dissolved in some nonre-active solvent, it is possible to electrochemically deposit out on an electrode when a current is passed through the solvated monomer. This has been accomplished with indene and acenapthalene. Another possibility is heating the monomer to form the polymer. Specifically, the heat supplies the thermal energy required to initiate the polymerization process and surmount the activation energy requirement E_A.

It was found that the easiest route to a polymeric material involved the direct addition of PA to PR under the conditions of reduced pressure heating and stirring.

additional sodium would not dissolve any further. The fresh sodium methoxide solution was suction filtered to remove traces of sodium hydroxide, a white solid, and mineral oil which had coated the raw metal. The flask was then tightly stoppered and stored for future use. The amount of sodium of sodium methoxide. The procedure used for the drying of methoxide formed was determined (19) by subtracting the weight of the flask plus methanol from that of the flask plus methanol plus sodium. The methanol was taken from Vogel and is as follows: genuine absolute methanol can be prepared from commercial methanol by treatment with magnesium activated by iodine. The dehydration is due essentially to magnesium methylate formation. The acid was added dropwise from a ground glass separatory funnel mounted on the reaction flask.

About 1.25g of, dry magnesium turnings and .125g of resublimed iodine were placed in a 500ml round bottomed pyrex flask and fitted with a double surface reflux condenser. 25ml of methanol was added through the condenser and the mixture warmed until the I_2 color disappeared. Vigorous evolution of H_2 was noted. 300ml of methanol was then added and the mixture boiled for a half hour under reflux. The product was distilled with exclusion of moisture and the first 25ml of distillate discarded. One drying treatment was found to be sufficient for the sodium methoxide reaction.

The sodium methoxide itself was made by adding shivers of raw metallic sodium piecewise to the dried methanol. Vigorous reaction was observed upon dissolution of the metal. It was necessary at times to cool the reaction with an ice bath when it became too vigorous. The apparatus used was a 250ml round bottom flask fitted with a reflux condenser and a $CaCl_2$ drying tube. The reaction was judged complete when

Additional sodium would not dissolve any further. The fresh sodium methoxide solution was suction filtered to remove traces of sodium hydroxide, a white solid, and mineral oil which had coated the raw metal. The flask was then tightly stoppered and stored for future use. The amount of sodium methoxide formed was determined by subtracting the weight of the flask plus methanol from that of the flask plus methanol plus sodium.

The next step was the formation of the sodium salt of propiolic acid. The acid was added dropwise from a ground glass separatory funnel mounted on the reaction flask- a 100ml round bottom vessel. It was found that immediate crystal formation took place along with the evolution of a large amount of heat. It became necessary to slowly add the acid over the period of one hour to the sodium methoxide solution, which was both constantly stirred and cooled in an ice water bath. The reaction vessel was kept cool due to the flammatory nature of the acetylene group contained in the acid. The crystals obtained were a pale cream color which slowly darkened to an orange-red hue upon exposure to light and air. The melting point was determined at 210 degrees centigrade. The crystals were suction filtered and dried in a vacuum desiccator until needed.

The scheme employed for the propiolic acid chloride synthesis presented some problems due to the extremely reactive, explosive nature of the triple bond. It was found that the easiest method placed the phosphorous oxychloride glass support. The same procedure was followed using TBO

and PA. This also gave a purple-red, semi-solid which hardened in a dry 100ml round bottom flask while the salt crystals were very slowly added to it over a four hour period. The mixture was stirred constantly using a magnetic stir bar and warmed slightly by a fiberglass heating mantle. Between and after additions, the reaction flask was attached to a reflux condenser equipped with a guard tube. After addition was complete, a few crystals of dry $\text{Ca}(\text{NO}_3)_2$ were added to enhance the phosphate precipitation and the mixture allowed to stand overnight. The resultant solution was vacuum filtered and the acid chloride- POCl_3 solution separated from the Na_3PO_4 . This mixture was then vacuum distilled by taking advantage of the differing vapor pressures of the two components. As POCl_3 has a higher vapor pressure than the acid chloride, it was preferentially frozen out in the distillation process.

Control Experiments

From infra red spectra, it was concluded that the amount of acid chloride obtained was small. Also complete separation from the POCl_3 was not obtained. It was decided to drop this route to the monomer when an alternate process was found to give good results. The thermal synthetic route to the polymer proved to be simpler than the above approach. The dye was added to the PA in a small flask while being stirred and heated under reflux. The resulting compound proved to be a polymer. With PR as the dye, the polymer is a very viscous, reddish-brown semi-solid which hardens upon standing in air on a glass support. The same procedure was followed using TBO

and PA. This also gave a purple-red, semi-solid which hardened to a film upon gentle heating on a glass support.

A property observed in both polymers is that heating above the reflux temperature resulted in spontaneous combustion of the sample, which is expected of poly(CH).

Another quality of these polymers is their thermoelasticity: they are able to be heated to the liquid state and then cooled to room temperature repeatedly with no observable change in their properties. Even at room temperature these films are malleable. This is an interesting finding as the literature reports poly(CH) as being a black, brittle polymer which is virtually insoluble in anything.

However, C.K. Chiang found that doped poly(CH) formed flexible films: Therefore a larger molecular "dopant" might conceivably increase this flexibility.

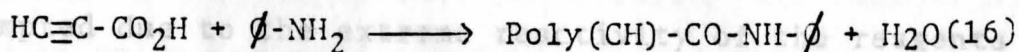
Control Experiments

It was not clearly shown spectroscopically that the polymer formed by reacting the dye and the PA is a poly(CH) molecule with amide linked dye pendant groups, as suggested by the synthetic scheme. Because of the difficulty in characterization associated with these polymers due to insolubility factors, viscosity and intense color, several control experiments were run in order to clarify these compounds by analogy with similar chemical substances.

The control experiments that were run duplicated the reaction conditions of the polymer synthesis. Heating under

reflux of the pure, neat PA gave no observable change in dye-poly(CH) compounds. its properties. This was verified by infra red spectroscopy; no noticeable change appeared in the acid spectrum both before and after reaction. As was expected, heating of the dyes in aqueous solution also gave no change in their properties.

Another control performed was that of reacting aniline with PA. A gold colored, brittle glass formed and an IR run confirmed the presence of an amide linkage. It was noted that this compound hardened more rapidly than the dye-PA polymer. The amide formation is given below:



It is interesting to note that this material, possibly polymeric, hardened much more rapidly than the poly(CH)-PR; suggesting that the smaller the "dye function (aniline)" the more brittle the polymer. Also noted was the rapidity of this reaction as compared to poly(CH)-PR: approximately one third of the time needed for poly(CH)-PR to form, possibly implying that the smaller the pendant group the faster the reaction time.

Other Controls: Propanoic Acid and Water Generation

Polymerization Type-Controls

There are three basic types of polymerization processes: cationic, anionic and free radical initiated mechanisms. Two of these types were tried on neat PA in order to possibly elucidate the specific process going on with the

dye-poly(CH) compounds.

Cationic polymerizations proceed by carbonium ion mechanisms, initiated by such compounds as sulfuric acid (H_2SO_4), boron trifluoride and iodine. ⁽²⁰⁾ H_2SO_4 was used as the catalyst initiator with PA, and we obtained no polymerization as the result. This is to be expected as it is not conceivable to form a carbonium ion of PA easily.

An anionic polymerization goes by way of carbanions as the propagating species. A common initiator is n-butyl-lithium. ⁽²⁰⁾ It is also known that electron withdrawing groups are easily polymerized by this mechanism. This reaction was not attempted due to the extreme reactivity of the reagents and the literature reports that poly(CH) is not usually polymerized by this system.

The last type of control polymerization technique tried was a free radical mechanism. Peroxides are good catalysts and we employed benzoyl peroxide activated by n,n-dimethylaniline. This reaction proceeds by free radicals generated by the initiator. When benzoyl peroxide was added to warmed, stirred PA no reaction was observed.

Other Controls: Propanoic Acid and Water Generation

Primulin was reacted with propanoic acid ($CH_3-CH_2-CO_2H$) under the same polymerization conditions with no reaction being the result. The dye could not be induced to undergo solvation during the course of the reaction.

One piece of information which is indicative of

an amide linkage formation during the polymerization, is the identification of water as a product. Referring back to eqn. 11, it is seen that water is formed from the reaction of the carboxylic -OH and the amine hydrogen. Droplets were observed to form on the upper inside of the vessel walls, and these were collected using a small pipette and placed on crystals of anhydrous blue silica gel. These drops decolorized the silica immediately, which is characteristic of water. Since neither of the starting materials (PR and PA) affected the silica gel in this way, it was concluded that water did in fact form during the polymerization reaction, and that it arose from an amide (an acid anhydride failed to form when PA was heated alone). The polymeric materials so tested were poly(CH)-PR, poly(CH)-TBO and poly(CH)-AN. These polymers were measured using the KBr method.

Poly(CH)-PR Comparison with PR

The spectra of PR and poly(CH)-PR as compared to PA (fig. 4.584) show the disappearance of bands at 790, 890, 1270, 1400 and 3350 cm^{-1} (characteristic of PA) when PA is incorporated in the polymer. The loss of the broad band at 3350 cm^{-1} is due to the loss of the -OH stretching function of the acid upon reaction. This is consistent with the loss of the C=O stretch at 1710 cm^{-1} . A less intense band at 790 cm^{-1} may be attributed to the out-of-plane bending of the -OH function, and its loss in the polymer spectrum is consistent

CHAPTER IV

EXPERIMENTAL THEORY, RESULTS AND DISCUSSIONInfrared Characterization

Infrared spectroscopy was used as a primary tool in characterizing the polymers, employing in all cases a Perkin-Elmer IR Spectrophotometer Model 700 A. Liquid materials were run neat, when possible, and the solid samples were run as pressed KBr pellets.

The control samples included neat propiolic acid (PA), Primulin (PR), Toluidine Blue-O (TBO), and aniline (AN). The polymeric materials so tested were poly(CH)-PR, poly(CH)-TBO and poly(CH)-AN. These polymers were measured using the KBr method.

Poly(CH)-PR Comparison with PR

The spectra of PR and poly(CH)-PR as compared to PA (fig. 4, 5 & 6) show the disappearance of bands at 790, 890, 1270, 1400 and 3350 cm^{-1} (characteristic of PA) when PA is incorporated in the polymer. The loss of the broad band at 3350 cm^{-1} is due to the loss of the -OH stretching function of the acid upon reaction. This is consistent with the loss of the C-O stretch at 1270 cm^{-1} . A less intense band at 790 cm^{-1} may be attributed to the out-of-plane bending of the -OH function, and its loss in the polymer spectrum is consistent

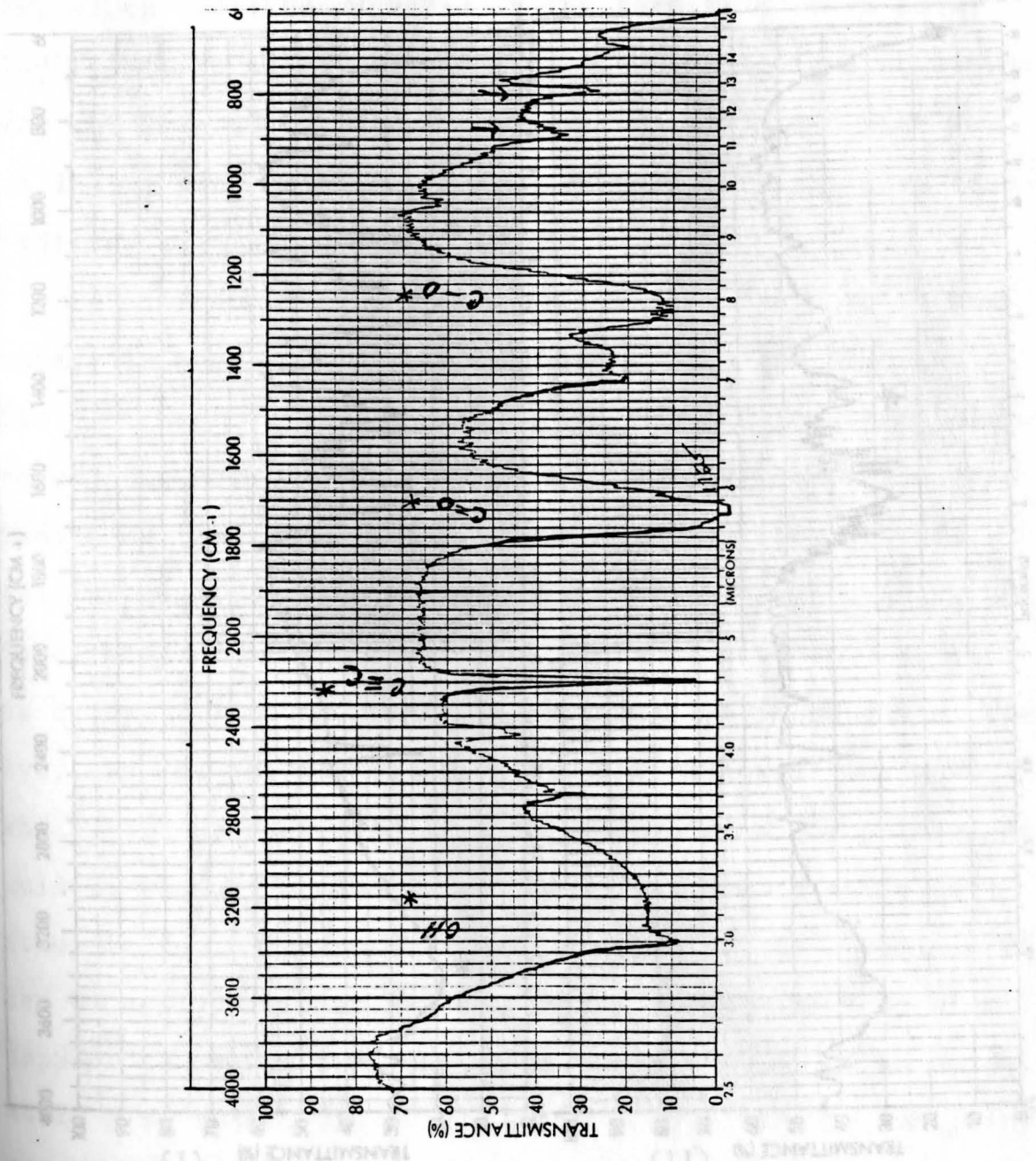


Fig.4: Infra red spectrum of neat propiolic acid.

* Refers to bonds which are characteristic only of the propiolic acid spectrum.

* New bands distinguished in the dye.

* New bands appearing in the polymer.

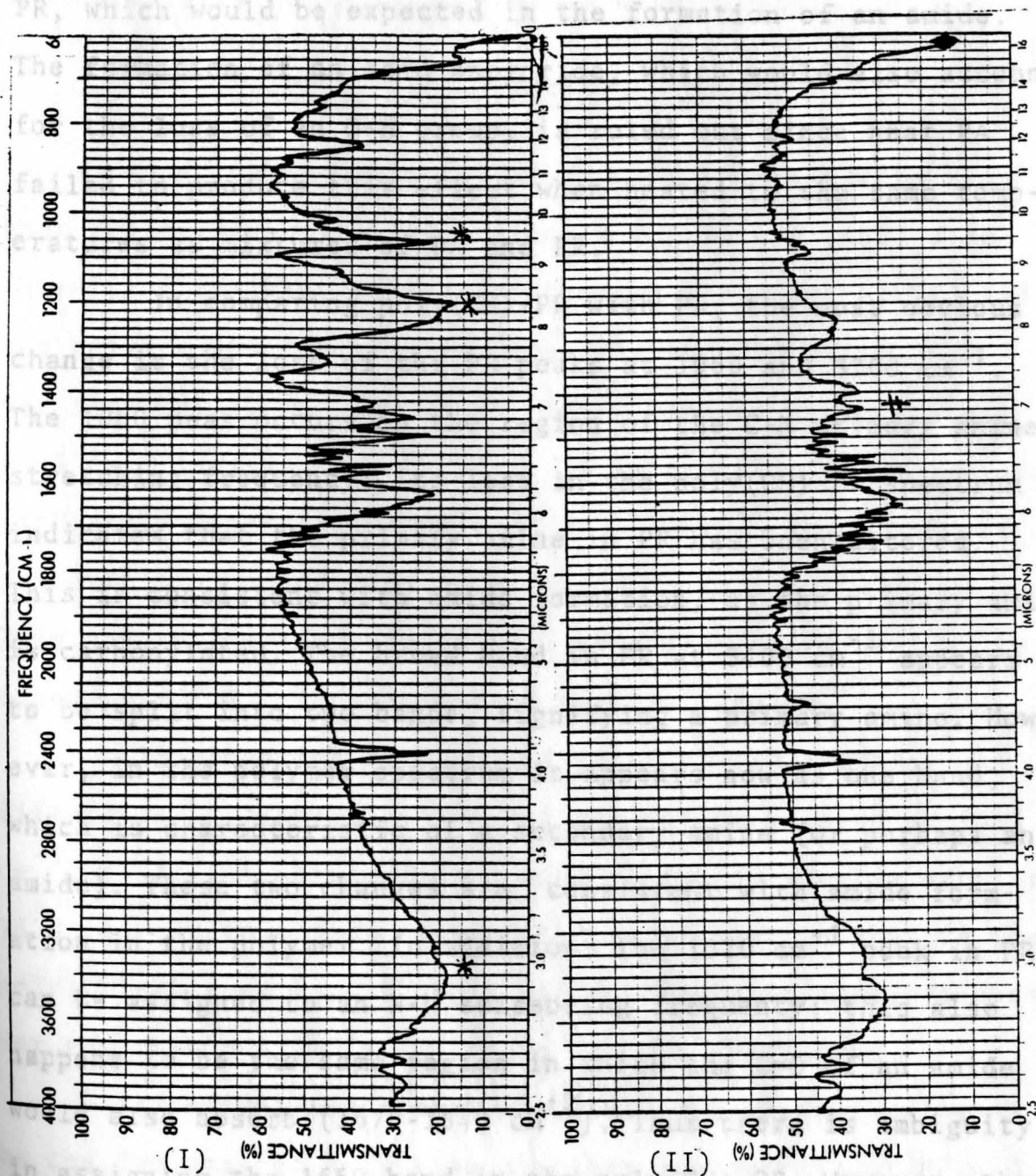


Figure 5: IR spectra of 1) Primulin and 2) Poly(CH)-PR.

* New bands distinguished in the dye.

New bands appearing in the polymer.

with the disappearance of the hydroxyl group. It is concluded that the hydroxyl function disappears on reaction with PR, which would be expected in the formation of an amide. The formation of an acid anhydride, which would also account for the loss of an O-H group, is ruled out since neat PA failed to produce this effect when heated to the same temperatures as mixtures of PA and PR.

In comparing poly(CH)-PR with PR, the most obvious change is the loss of the PR peaks at 1060 and 3200 cm^{-1} . The 1060 peak occurs in the region of the C-N primary amine stretching frequency; its loss in the poly(CH)-PR spectrum indicates that the primary amine in PR has been altered. This is consistent with amide formation, as the primary amine is carbonylated. The broad band in PR at 3400 cm^{-1} appears to be split into two bands, signifying a primary amine. However, in the polymer spectrum it appears now as one band, which is characteristic of a secondary amine (or perhaps an amide). These two changes are consistent with amide formation in the polymer. In addition, the 1620 cm^{-1} peak in PR can be assigned to an N-H scissoring frequency; this also happens to be the same region in which the C=O of an amide would also absorb (1670-1640 cm^{-1}). Thus there is ambiguity in assigning the 1650 band in the poly(CH)-PR. However, the evidence is still consistent with amide formation.

Another striking loss is that of the acetylenic triple bond of PA in the poly(CH)-PR spectrum. Obviously, the triple bond has been lost due to the amide synthesis, and

the formation of a conjugated double bond system is suggested as there are absorptions at 1600 and 3000 cm^{-1} , which are characteristic for a carbon-carbon double bond.

Poly(CH)-TBO Comparison with TBO

Now looking at poly(CH)-TBO and PA, it can be seen that again the hydroxyl function is completely lost; also there is a striking similarity between the poly(CH)-TBO and the poly(CH)-PR spectra. In comparing the TBO and PR polymer spectra, the suggestion of a new band at approximately 1385 cm^{-1} is seen in both. This is interesting, as Heeger and MacDiarmid report a narrow band at 1370 cm^{-1} which they attribute to an absorption mode in semiconducting poly(CH). This absorption is found to be a general feature of lightly doped poly(CH), independent of specific dopant.⁽²³⁾

In comparing the TBO and poly(CH)-TBO spectra, one difference is clear: the N-H scissor in TBO is seen at 1625 cm^{-1} , while the corresponding band in the polymer is seen at 1650 cm^{-1} , with a much broader shape, similar to that in the poly(CH)-PR spectrum. This is interpretable as more evidence for the carbonyl C=O of an amide linkage formation.

A control experiment performed was that of using AN as the dye analog. AN is the simplest counterpart of PR and TBO. Looking at the aniline polymer as compared to the acid spectra; the same general pattern is followed: loss of the O-H function on the acid, loss of the $-\text{NH}_2$ peaks, and downshifting of the acid carbonyl in the poly(CH)-AN. It is again

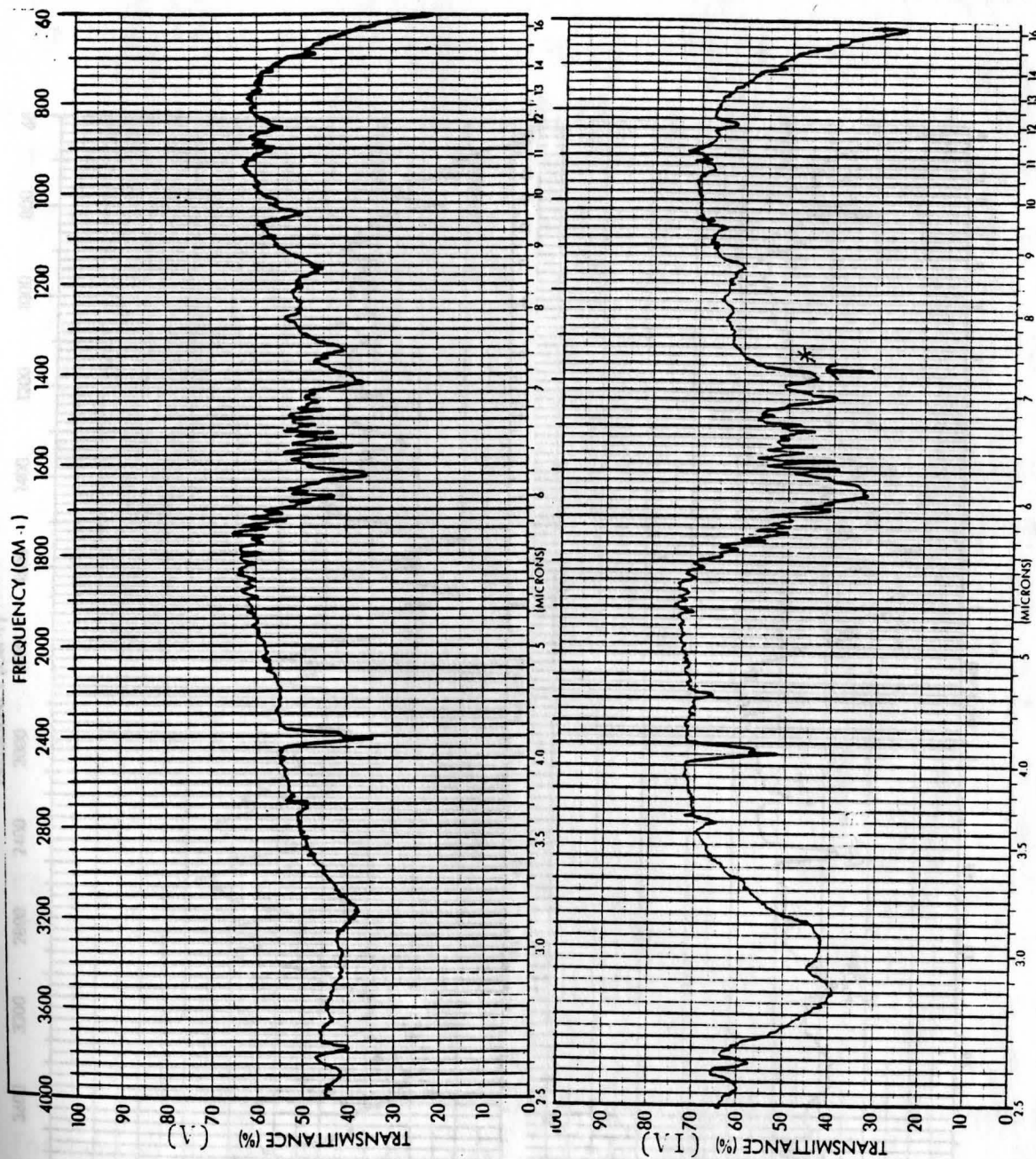


Figure 6 : IR spectra of 5) Toluidine Blue-O and 6) Poly(CH)-TBO.

* Possible new band marked in the polymer spectrum.

Figure 7 : IR spectra of 3) Aniline and 4) Poly(CH)-AN.

* New band often found in poly(CH) materials which are lightly doped.

obvious that the hydroxyl function has been altered, possibly in water formation. Comparison of the neat AN spectrum with that of the polymer shows a secondary amine formation in the change of the absorption at 3400 cm^{-1} in AN

In comparing all three of the polymer spectra

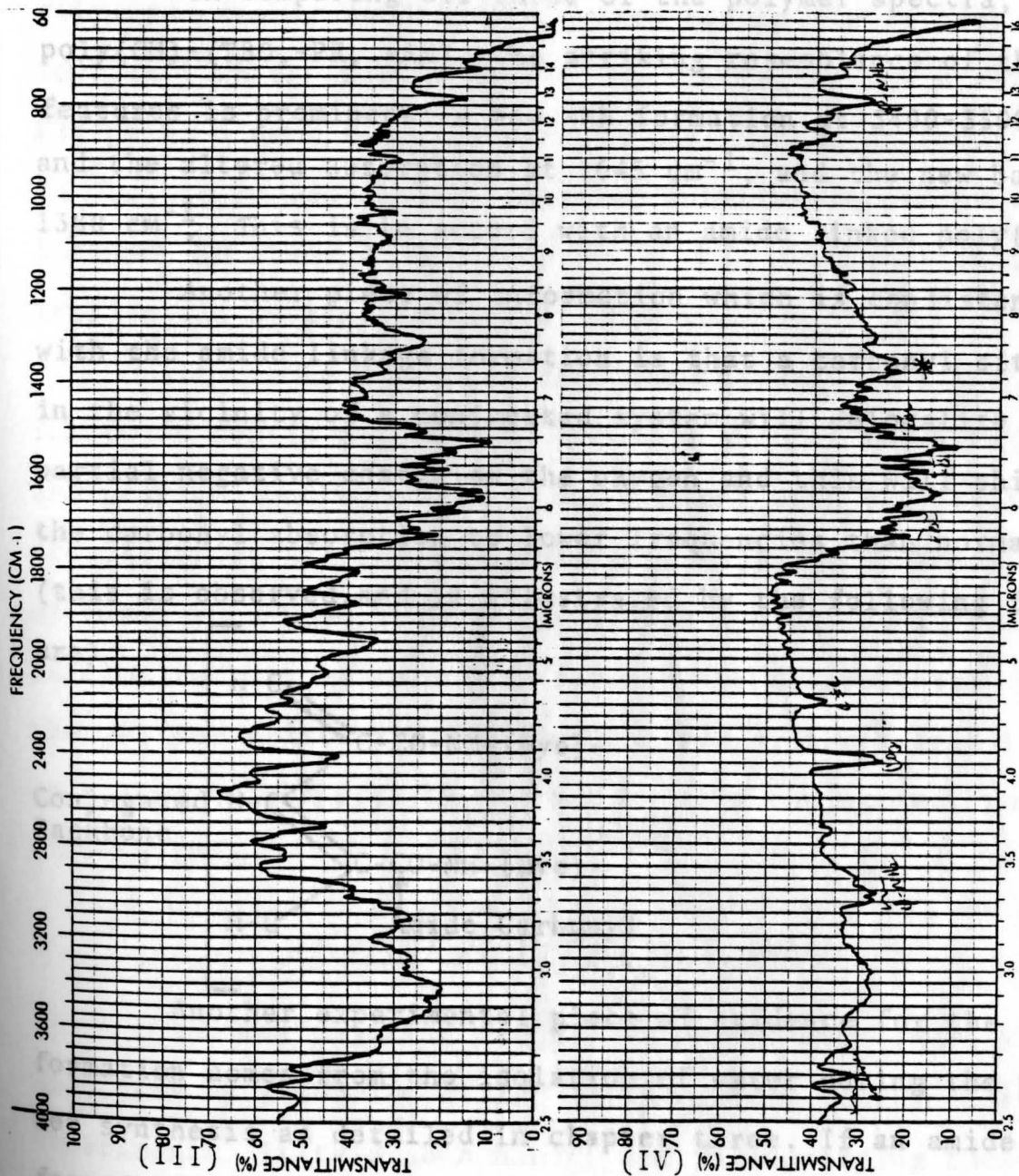


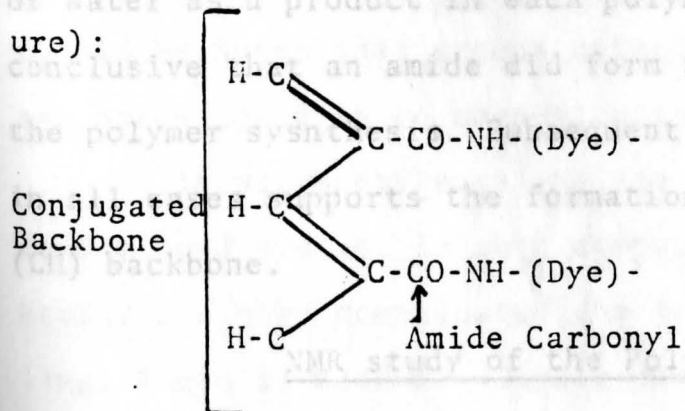
Figure 7.: IR spectra of 3) Aniline and 4) Poly(III)-AN.

* New band often found in poly(III) materials which are lightly doped.

obvious that the hydroxyl function has been altered, possibly in water formation. Comparison of the neat AN spectrum with that of the polymer shows a secondary amine formation in the change of the absorption at 3400 cm^{-1} in AN

In comparing all three of the polymer spectra, poly(CH)-(TBO,-PR, -AN), the striking resemblance of their features is prominent: a new -NH formation at $3400\text{-}3500\text{ cm}^{-1}$, and the altered absorption at 1645 cm^{-1} , and the new band at 1380 cm^{-1} . This is in accord with an amide linked poly(CH).

Another piece of information which is consistent with the amide linkage formation is that a carbonyl situated in the vicinity of a conjugated system will delocalize the partial negative charge on the oxygen and this will shift the carbonyl absorption to lower frequencies than normal (this is observed, and is illustrated by the following figure):



Another experimental piece of evidence for the amide formation comes from the isolation of water during the polymer synthesis as detailed in chapter three. If an amide is formed, then water is one of the products. So, this is consistent with the loss of the hydroxyl acid function in all of the polymer spectra.

Concerning the formation of the polymeric backbone, it is strikingly seen in all three polymer spectra that the $\text{C}\equiv\text{C}$ absorption is lost at 2150 cm^{-1} . This confirms the loss of the triple bond during the polymer synthesis. Unfortunately, the doubly bonded, conjugated absorption is seen at 1600 cm^{-1} which also happens to be the region for a strong KBr peak. A double bonded peak should be seen at about 3000 cm^{-1} . This region also is somewhat interfered with by the intense -NH absorptions. However, the loss of the triple bond in all systems is clearly observed.

It can be concluded that the infrared spectral evidence is consistent with an amide linkage of the dyes to the poly(CH) backbone. This, taken along with the striking similarity of all three polymer spectra, and the isolation of water as a product in each polymer synthesis, is fairly conclusive that an amide did form as the desired product of the polymer synthesis. Subsequent loss of the triple bond in all cases supports the formation of a conjugated, poly-(CH) backbone.

NMR study of the Poly(CH)-Dyes.

Nuclear magnetic resonance spectroscopy (nmr) was used both as a characterizing and a kinetic tool in these experiments. It is also a useful aid in supporting the conclusions deduced from the IR spectra. Together, these two techniques were employed to do the major characterizat-

ion of the materials. The monomers were difficult to work with due to their low solubility, even in aqueous media, and the polymers were even less soluble.

In TBO and PR, nitrogen is incorporated in a heterocyclic ring system and in a primary amine function. It is known that most nitrogen compounds undergo a quadrupole broadening effect when irradiated with NMR frequencies. In some compounds, especially pyrroles and other heterocycles, the -NH resonance can be subject to such a large broadening effect that it is difficult to distinguish the absorption from the baseline of the spectrum. This appears to be the case with the amide -NH resonance in the spectra of the poly(CH)-dyes. What -NH absorptions are discernable in the dyes' spectra are lost in the subsequent polymer spectra, presumably due to this effect. Also, while discussing amides, it should be noted that groups attached to an amide nitrogen are often found to be magnetically nonequivalent. (18)

In polyacetylenes, we are dealing with a conjugated, double bond system. In such compounds, the NMR spectra generally are more complicated due to vicinal and geminal coupling. There is also an allylic coupling effect associated with multi, doubly bonded systems. The overall effect is that the NMR spectra of the polymers is fairly complicated to interpret.

In the PR spectrum, the ring hydrogens can be identified around 6 ppm, with the expected broadening effect due to the presence of the nitrogen heterocycles adjacent to the

phenyl hydrogens. The other identifiable peak is at about 2 ppm, and this is thought to be the methyl hydrogen resonance, which is consistent with an expected downfield shift deshielding, due to the delocalizing effect of the large ring system.

The TBO system shows a clear phenyl hydrogen resonance at 7 ppm with the two methyl groups appearing downfield at 1 and 2.5 ppm respectively. The phenyl methyl is located downfield at 2.5 ppm again due to the delocalizing effect of the rings, and the nitrogen dimethyl group is assigned the 1 ppm peak. It is difficult to assign the primary amine hydrogens in this spectrum due to the broadening effect referred to earlier.

Spectra were run of the heated (PR + PA) mixtures at progressive time intervals during the polymerization. The most notable features were an extreme broadening of the acetylenic resonance at 3 ppm as the reaction proceeded and the gradual decrease of an amine resonance near 1 ppm. This large broadening of the acetylene absorption shows a very good resemblance to spectra of polyindene obtained by Mano and Calafate⁽¹⁹⁾ and also to a broad resonance seen in a trans poly(CH)⁽²²⁾ spectrum from work done by Clarke et.al. Two reasons are postulated here for this effect: 1) during the progress of the reaction, the spectrometer is seeing a mixture of triple bonds being reduced to a conjugated system of interchanging double and single bonds, the result of which is the observed broadened resonance of this transient equilibrium

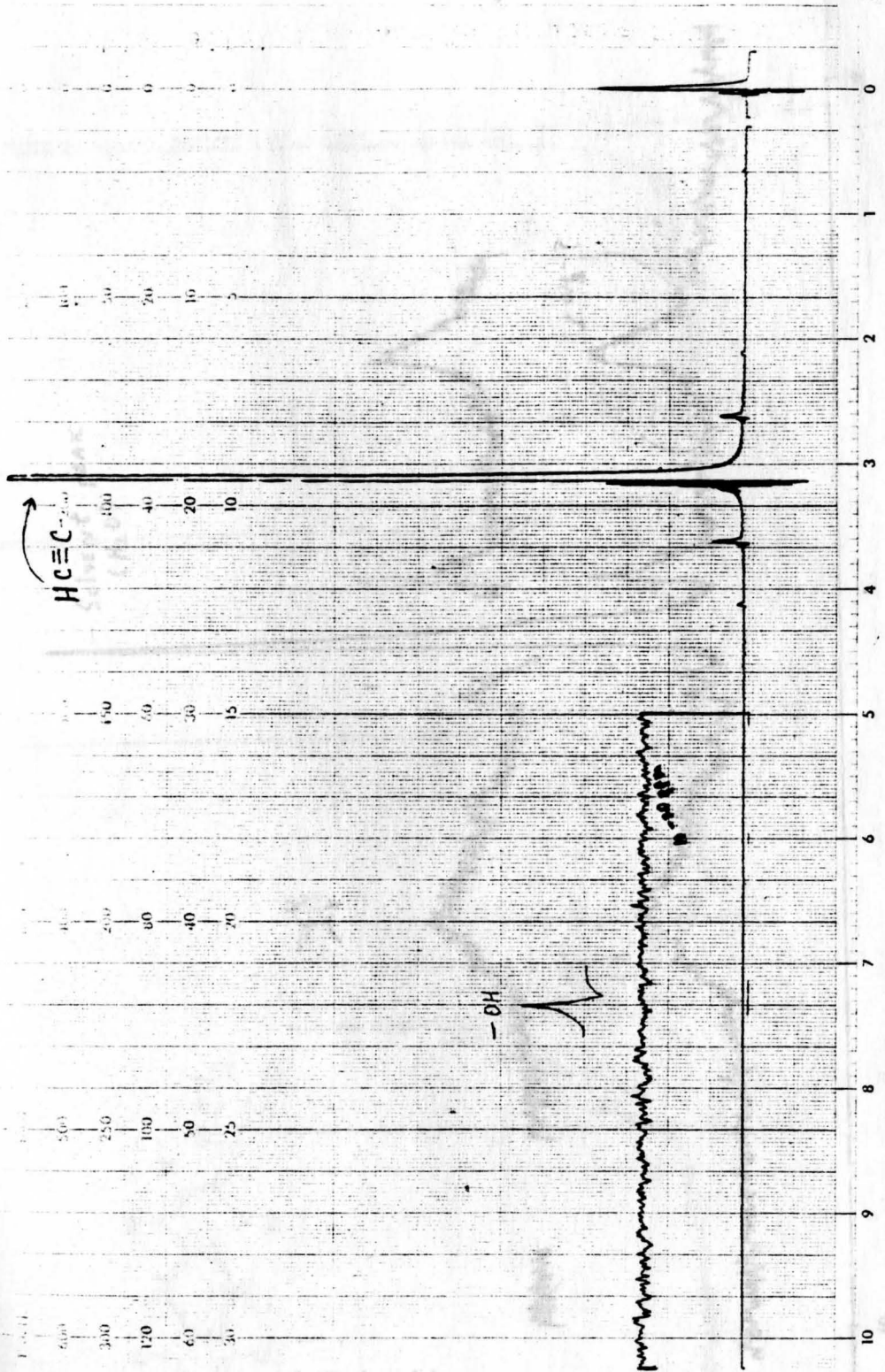


Fig.8: NMR spectrum of neat propionic acid.

(c)

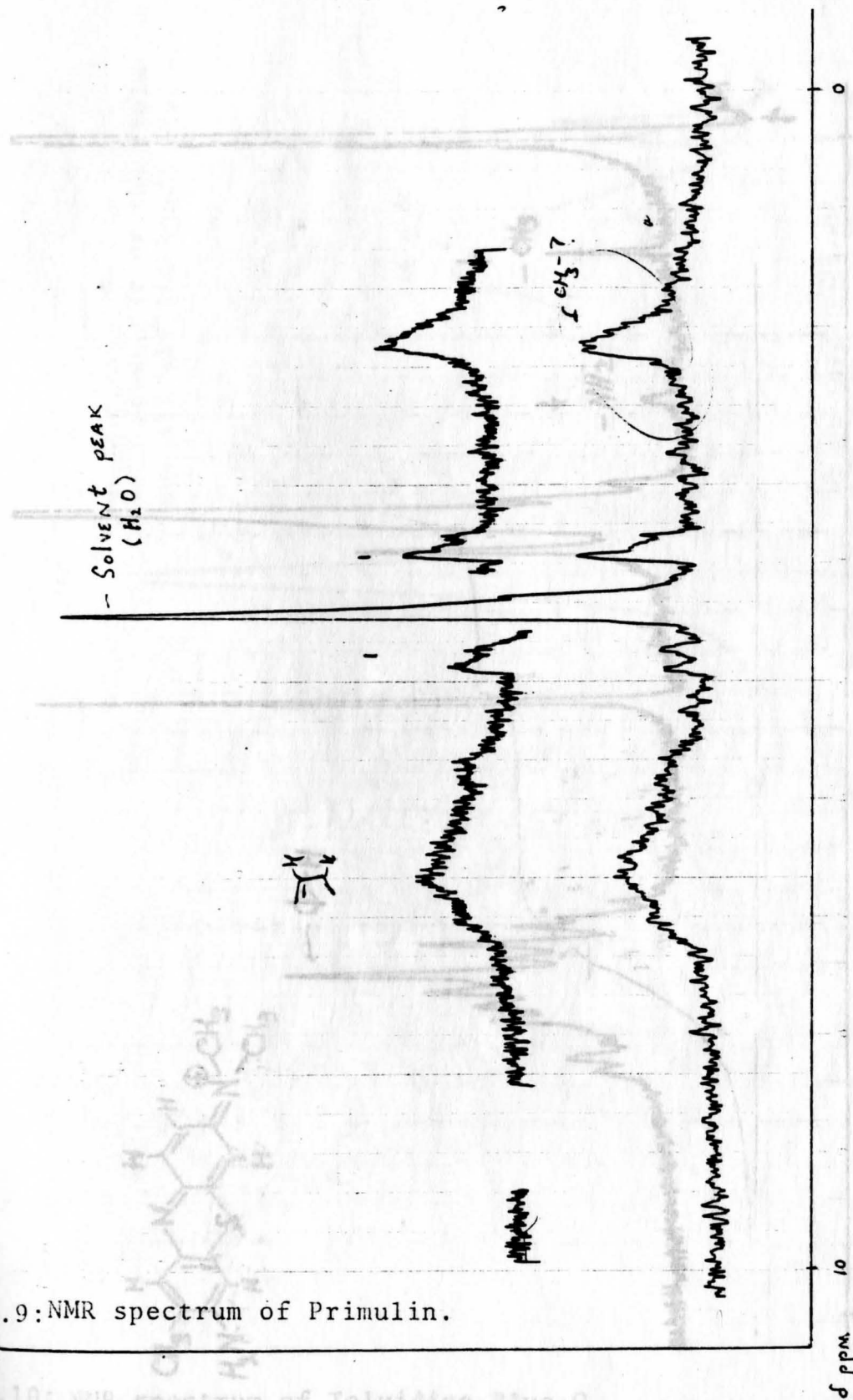


Fig.9: NMR spectrum of Primulin.

Fig.10: NMR spectrum of Toluidine Blue-O.

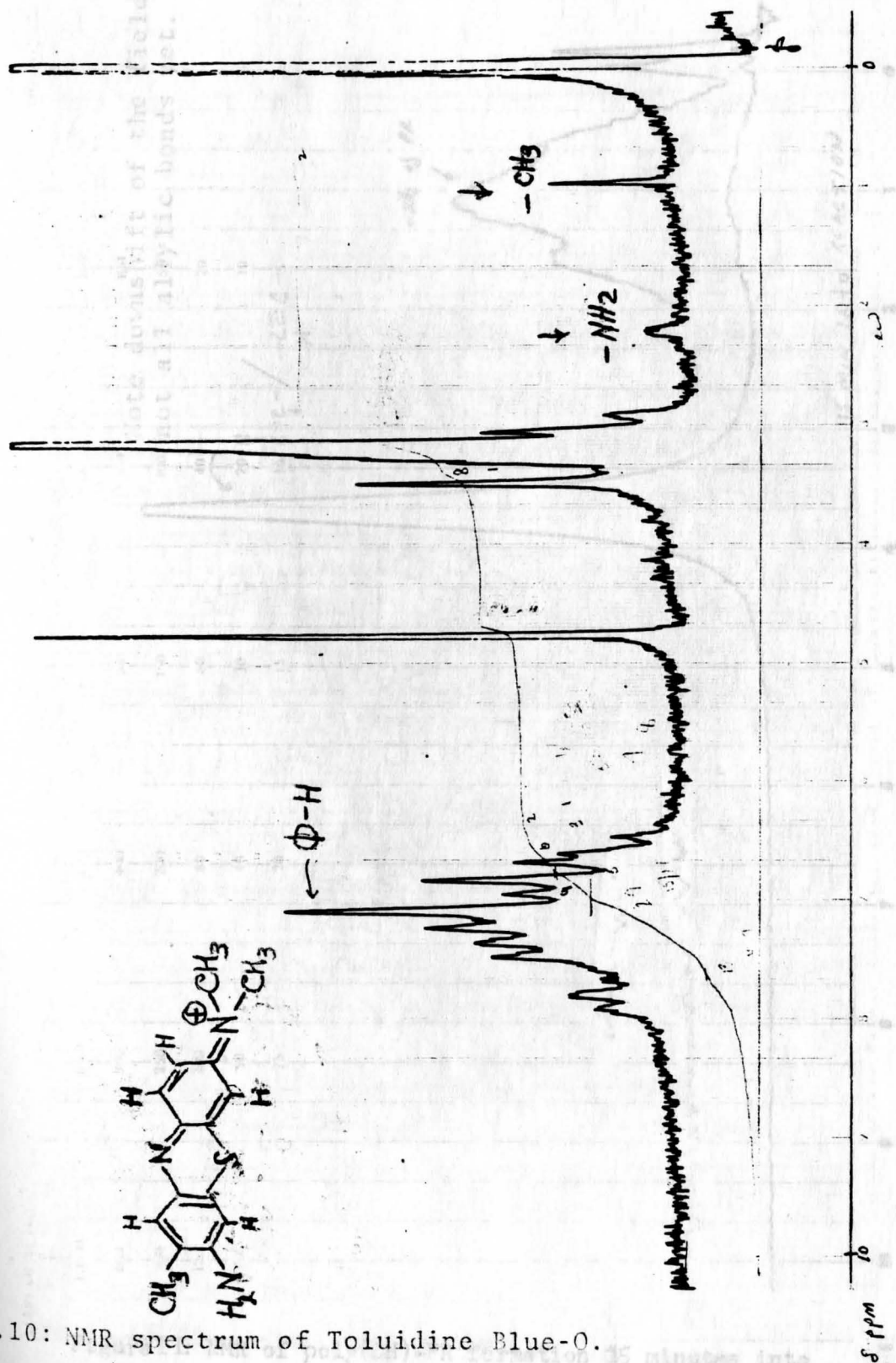


Fig.10: NMR spectrum of Toluidine Blue-0.

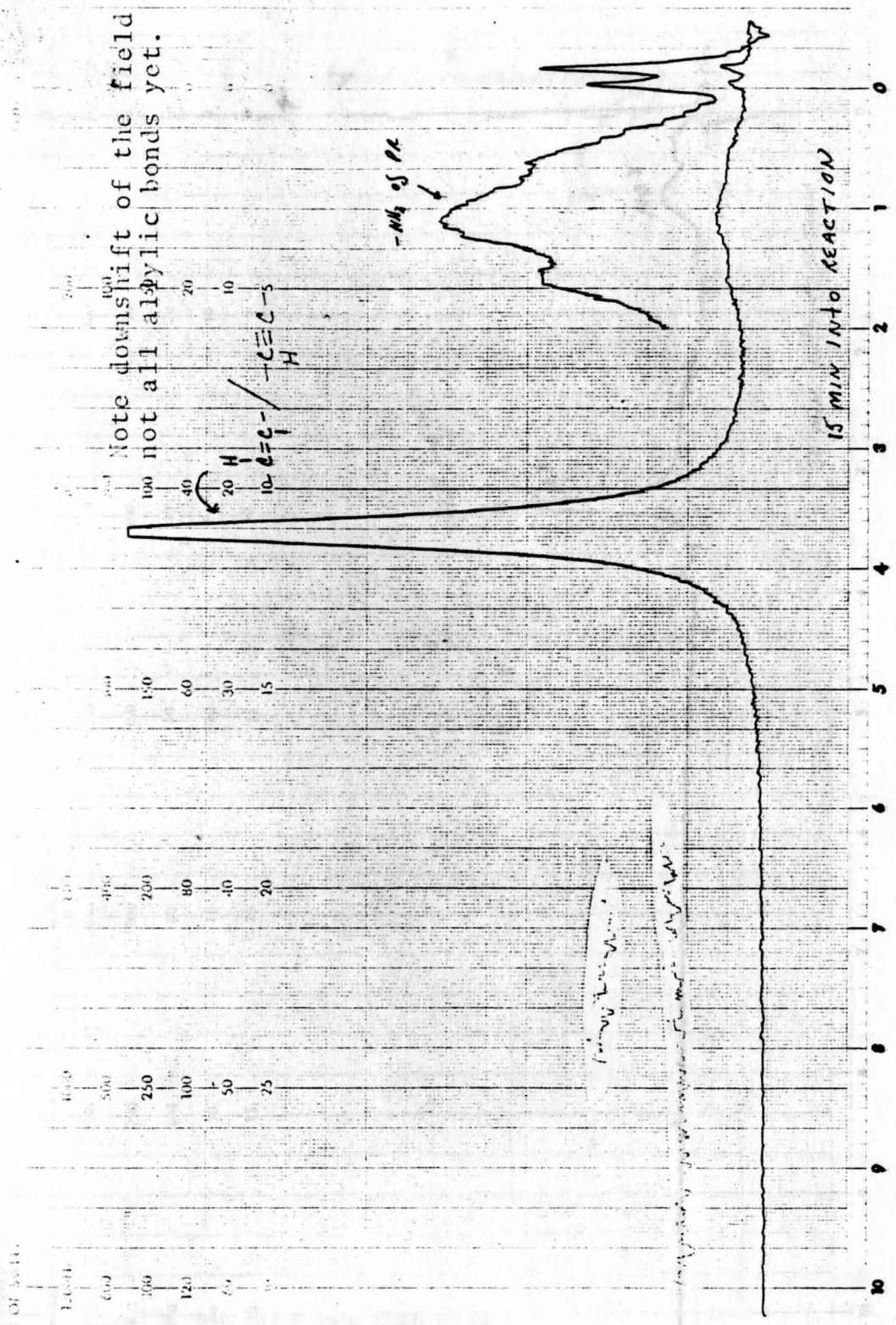


Figure 11: NMR of poly(CH)-PR formation 15 minutes into the reaction.

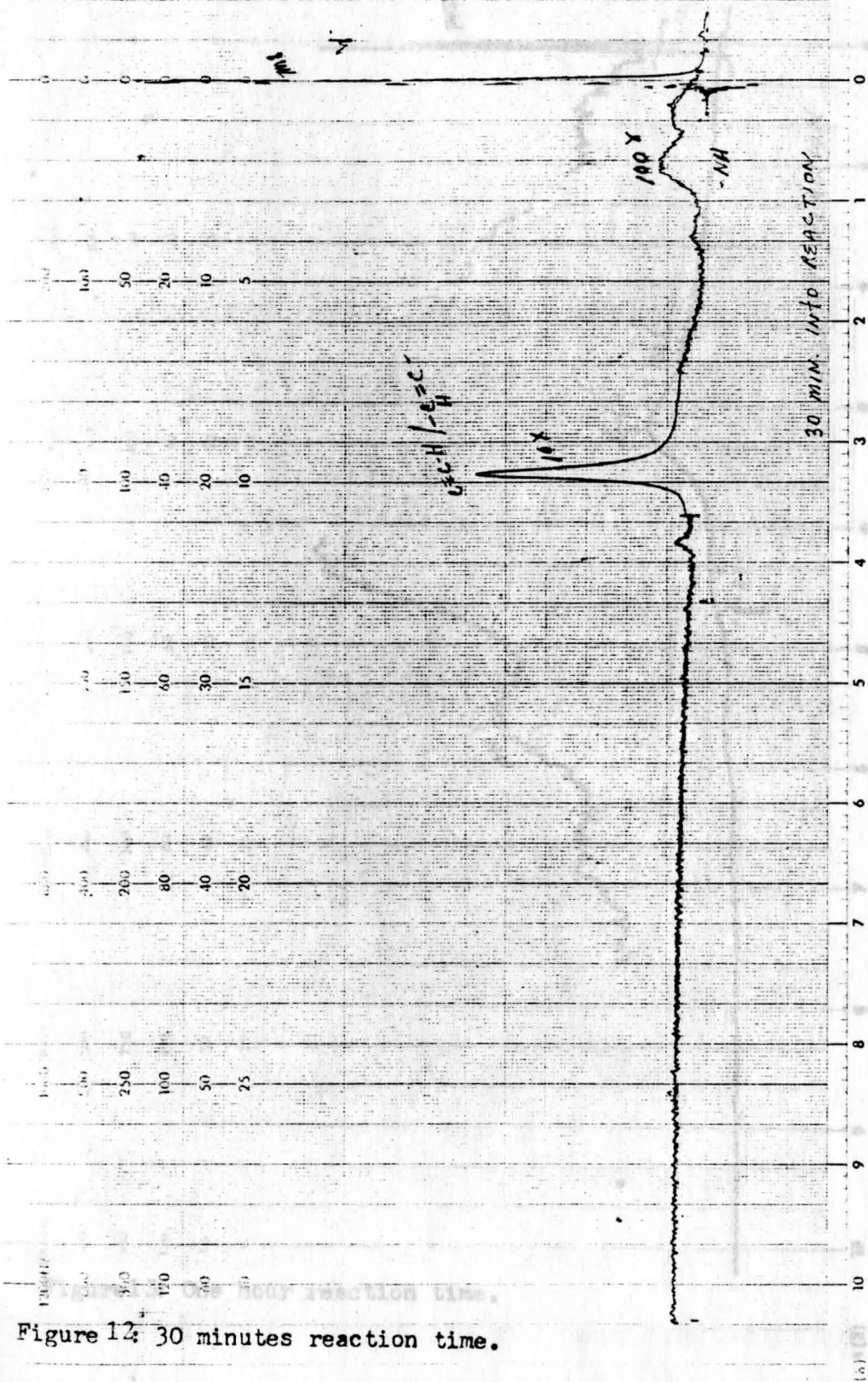


Figure 12: 30 minutes reaction time.

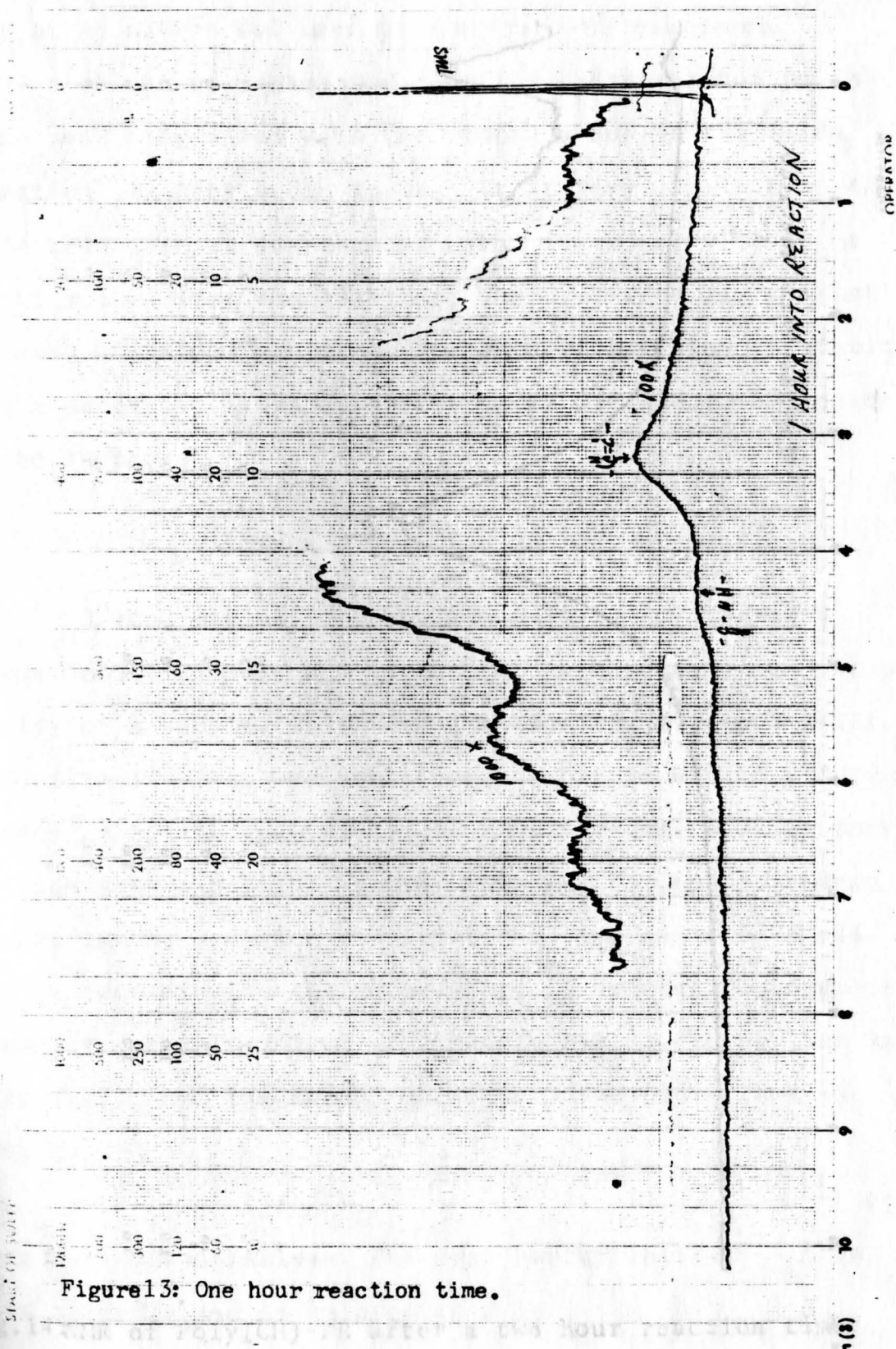


Figure 13: One hour reaction time.

between the two types of bonds; and 2) the downfield shift of the broadened peak toward the more characteristic frequencies of an alkene and loss of the free -OH resonance.

postulated: the disappearance of the amine peak progresses with the reaction due to the formation. As previously stated, it is very likely that the amine resonance is so broadened that it is distinguished from the broad resonance of the water in the spectrum.

A good reaction was observed in the polymer conversion. The solubility of a sample of poly(CH)₂-PR or "soliton" This was a balance of 6.1 g sample in conjunction with 100 ml of weights in the presence of a magnetic field.

According to the theoretical treatment of the magnetic moment, the value of the magnetic field, and the magnetic field given by

where χ is dimensionless. The gram susceptibility is related to χ by

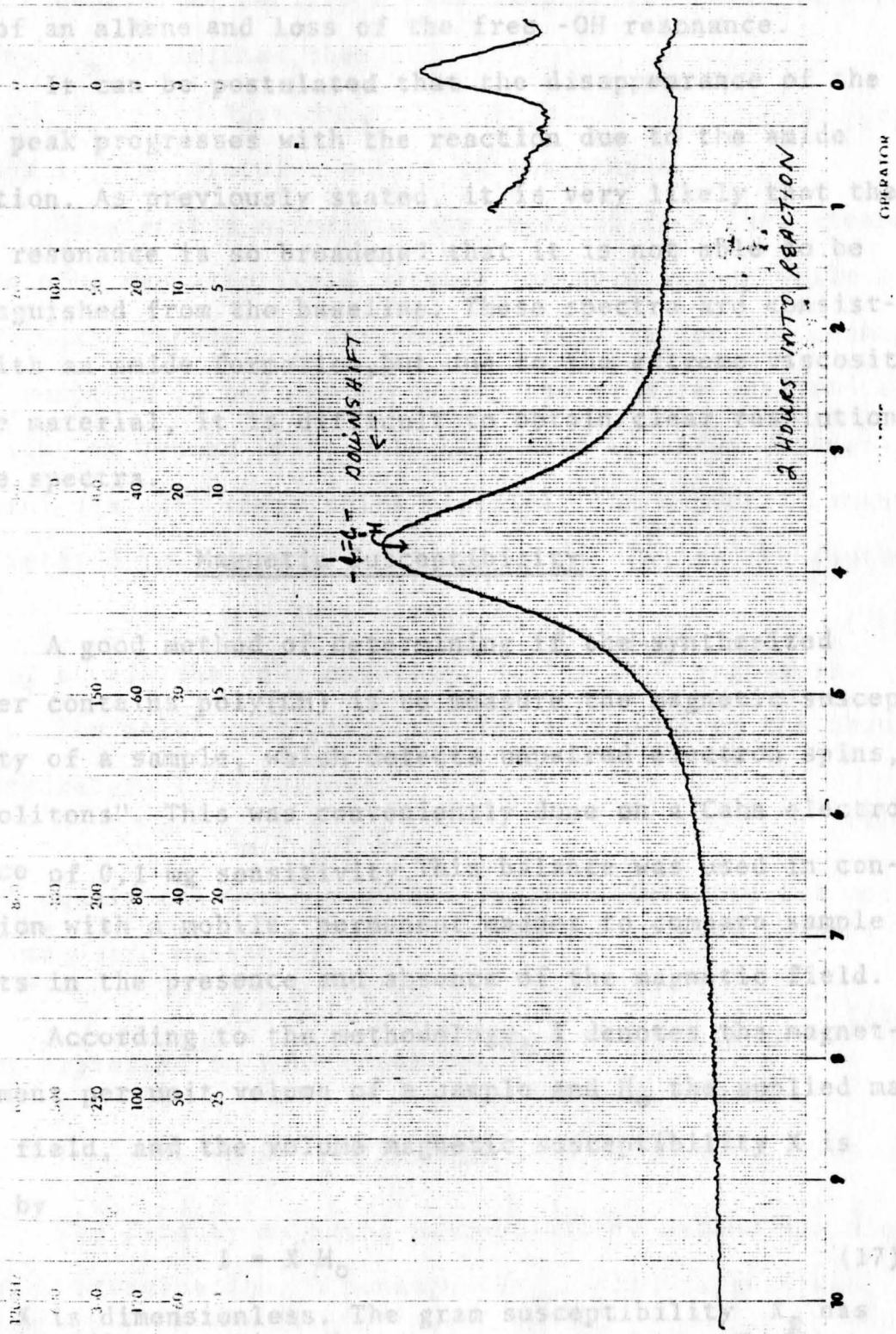


Fig. 14 NMR of Poly(CH)₂-PR after a two hour reaction time.

between the two types of bonds; and 2) the downfield shift of the broadened peak toward the more characteristic frequencies of an alkene and loss of the free -OH resonance.

It can be postulated that the disappearance of the amine peak progresses with the reaction due to the amide formation. As previously stated, it is very likely that the amide resonance is so broadened that it is not able to be distinguished from the baseline. These spectra are consistent with an amide formation, but due to the extreme viscosity of the material, it is difficult to obtain clear resolution in the spectra.

μ is related to Magnetic Susceptibility (χ) by the equation:

$$\mu = (n(n+2)) \frac{B_B}{2} \quad (20)$$

A good method of determining if the synthesized polymer contains poly(CH) is to measure the magnetic susceptibility of a sample, which detects unpaired electron spins, or "solitons". This was conveniently done on a Cahn electro-

balance of 0.1 mg sensitivity. This balance was used in conjunction with a mobile, permanent magnet to compare sample weights in the presence and absence of the magnetic field.

According to the methodology, I denotes the magnetic moment per unit volume of a sample and H_0 the applied magnetic field, and the volume magnetic susceptibility χ is given by

$$I = \chi H_0 \quad (17)$$

where χ is dimensionless. The gram susceptibility χ_g has units of cm^3/g and is related to χ by

obtained. Then the $X_g = X/P$ (18)

where P equals the density of the sample. The molal susceptibility X_m is defined then as

obtained. The same $X_m = M X_g$ (19)

where M is the molecular weight of the sample.

Diamagnetic materials are repelled from the intense region of a magnetic field between the pole faces, while a paramagnetic sample is attracted to this region. A paramagnetic compound is defined as having one or more unpaired e^- , requiring in ground state molecules that e^- enter degenerate orbitals with their spins parallel. The magnetic moment μ is related to the number of unpaired e^- (n) by the equation:

$$\mu = (n(n + 2))^{1/2} B_b \quad (20)$$

where B_b equals the Bohr magneton: 9.27×10^{-2} erg/gauss.

The molal susceptibility X_m is related to the absolute temperature T as follows:

$$X_m = A + C/T \quad (21)$$

where C equals the Curie constant and is related to the molecular magnetic moment by

$$\mu = 2.824 C^{1/2} \quad (22)$$

μ being expressed in Bohr magnetons. (21)

Procedure

The Faraday magnetic susceptibility method was used for this determination. A nonmagnetic gelatin capsule was weighed both in and out of the magnetic field by the electrobalance until a steady weight fluctuation of ± 0.05 mg was

obtained. Then the standard calibrating sample of $\text{Hg}(\text{Co}(\text{NCS})_4)$ was added to the capsule and weighed both in and out of the field until a constant weight difference was obtained. The same procedure was followed for the poly(CH)-dye samples.

The X_g of the standard is given by the equation

$$X_g = \frac{4.985 \times 10^{-3}}{(T-2)} \quad (23)$$

where T is the room temperature expressed in degrees Kelvin.

Knowing the standard value, X_g of the unknown sample can be calculated from the following relation:

$$(24) \quad X_{g(\text{sample})} = X_{g(\text{std})} \times \left[\frac{\text{weight}(\text{sample})}{\text{weight}(\text{std})} \right] \left[\frac{\text{weight}(\text{std})}{\text{weight}(\text{sample})} \right]$$

Since $X_m = M X_g$ then $X_g = X_m/M = A + C/T$. A is small enough that it can be neglected, so the following relation is obtained:

$$X_g = CT/M. \quad (25)$$

$$\text{Since } C = (u/2.824)^2, \text{ then} \quad (26)$$

$$X_g = u^2/TM(2.824)^2. \quad (27)$$

Therefore, in equation 27, the only variable which needs to be estimated is M. The molecular weight of the polymer is estimated as follows; poly(CH) is known to contain 12-16 CH units on the average⁽⁸⁾, so a lower weight was taken to be 8 CH units and an upper weight 16. Using these approximations, the molecular weights were calculated assuming only one PR molecule to be attached per poly(CH) chain (as given by the mole ratio of the reactants). Thus, the lower weight became 516 g/mole and the higher, 620 g/mole. Using these approximations, the number of unpaired e^- per poly(CH)-PR chain

and number = 0.47 unpaired e⁻/poly(CH)-PR chain.
 could then be directly calculated using equation 27

These results indicate the existence of a reasonable

number of unpaired Data and Calculations which supports the

RT=27.6 C

Sample	Net Weight(mg)	H ₀ Weight(mg)	Difference
Hg(Co(CNS) ₄)	39.10	36.00	3.10
	39.10	35.90	3.20
	39.05	35.95	3.10
Average	39.08 ± .02	35.95 ± .02	3.13 ± .03

Poly(CH)-PR Sample 1	92.30	92.7	.40
	93.10	93.5	.40
	93.10	93.5	.40
	92.73	93.5	.40

Sample 2	90.80	91.20	.40
	90.80	91.20	.40
	90.55	90.90	.35
	90.60	90.90	.30
	90.70 ± .06	91.05 ± .08	.36 ± .02

$$X_g(\text{std}) = \frac{4.985 \times 10^{-3}}{298.75} = 1.67 \times 10^{-5}$$

$$X_g(\text{S1}) = 1.67 \times 10^{-5} (.37/3.13 \times 39.08/90.70)$$

$$= 8.50 \times 10^{-7} \text{ cm}^3/\text{g. lose } e^- \text{ (oxidation).}$$

$$X_g(\text{S2}) = 1.67 \times 10^{-5} (.38/3.13 \times 39.08/92.73)$$

$$= 8.43 \times 10^{-7} \text{ cm}^3/\text{g.}$$

Thus, the average X_g of poly(CH)-PR = 8.46 x 10⁻⁷ cm³/g.

Assuming M for the polymer gives

$$X_m = 516((8.46 \pm .03) \times 10^{-7}) = 4.40 \times 10^{-4} \text{ and}$$

$$X_m = 620((8.46 \pm .03) \times 10^{-7}) = 5.50 \times 10^{-4}.$$

Using the previously derived relations, n_{lower} and n_{upper} can be calculated and given the following values:

$$n_{\text{lower}} = 0.42 \text{ unpaired } e^-/\text{poly(CH)-PR chain}$$

and $n_{\text{upper}} = 0.47$ unpaired e^- /poly(CH)-PR chain.

These results indicate the existence of a reasonable number of unpaired e^- in our polymer, which supports the conclusion that a poly(CH)-backbone is present in our sample of poly(CH)-PR. Such verification was not attainable in the case of poly(CH)-TBO, though the existence of amide linkages and a poly(CH) backbone was suggested earlier.

Cyclic Voltammetry

Cyclic Voltammetry (CV) was the method employed for characterizing the electrochemical behaviour of the poly(CH)-PR. Voltammetry can be used to analyze any chemical species that is electroactive i.e. that can be made to undergo oxidation and/or reduction. In this technique, the potential of the electrode is the controlled parameter which causes the chemical species to be oxidized or reduced. The potential can be seen as "electron pressure" which forces a species in solution to gain e^- (reduction) or to lose e^- (oxidation). As the potential of the electrode becomes more negative, it becomes more strongly reducing. Conversely, as the potential becomes more positive, the electrode becomes more oxidizing (see fig. 14). Therefore, the redox reaction taking place on the electrode can be regulated by controlling the electrode potential.

The current (i) is a measure of the e^- flow. The current is due to e^- transfer which takes place when an oxidation or reduction takes place on the electrode surface

(or in the electrolyte layer next to the electrode). This redox current is proportional to the concentration of the electroactive species in the vicinity of the electrode.

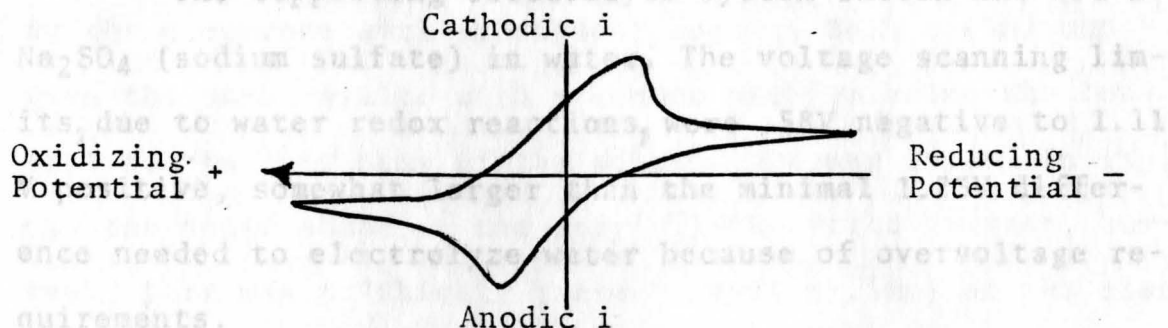


Figure 15: Convention for plotting a cyclic voltammogram.

Experimental

The equipment used to measure the CV plots consisted of a Model 364 Polarographic Analyzer power source which was regulated by a Wavetek Model 142 HF VCG waveform generator. The voltammograms were monitored by a Valtec Model 1024 X-Y recorder and the potential applied to the working electrode was registered by a Sabtronics Model 2010A digital multi-meter.

The electrodes used were made by attaching a thin platinum sheet to a glass support with silver epoxy manufactured by Acme chemicals. Silicon caulking made by General Electric products insulated the silver layer from contact with the solution. The cell itself was a triple compartmented flask separated by porous glass frits. Quartz windows in each of the compartments allowed illumination of the immersed elec-

trodes. The electrodes employed included a Pt polymer coated working electrode, a silver counter electrode and a standard (SCE) reference electrode.

The supporting electrolyte system chosen was 0.1 M Na_2SO_4 (sodium sulfate) in water. The voltage scanning limits, due to water redox reactions, were .58V negative to 1.11 V positive, somewhat larger than the minimal 1.23V difference needed to electrolyze water because of overvoltage requirements.

The naked Pt electrodes were used to measure a CV in order to determine the exact nature of the solvent window for that particular electrode. Other control electrolytes used in Na_2SO_4 included HgSO_4 , NiCl_2 and FeSO_4 . The redox potentials of these metals were determined in order to see if there was any uptake of the cations into the plated polymer-electrolyte system. If there was, an increase in the metal redox peak over time would be observed. This is due to the metal cation being incorporated into the polymer layer, effectively increasing its surface concentration with time.

Other controls tested were PA, TBO and PR in Na_2SO_4 , respectively. TBO and PR are essentially nonelectroactive; their CV's are identical to that of the supporting electrolyte used. Propiolic acid, however, shows a reducing potential at -.58V and an oxidized and reduced species at about +.18V, perhaps caused by Kolbe reactions and the reduction of the $\text{C}\equiv\text{C}$. See the following four voltammograms, pp.55-58.

There were two methods employed in coating the polymer on the electrode: 1) dip coating was used involving heating of the poly(CH)-PR with the electrode immersed in the heating vessel; and 2) spreading of the warm material on the electrode with subsequent drying. Both techniques gave the same results with a common problem being the control of the thickness of the adhered polymer layer. In fig. 19, the basic shape of the poly(CH)-PR cyclic is seen, however, this was a "thickly coated" layer (.5mm) on the electrode and this is reflected by the increasing conduction buildup with time. This observation is supported by the work done by Diaz and Castillo, who have found that CV's run on thick films slow the electrochemical reaction and also considerably broaden the peaks.⁽¹⁵⁾ In the thin layer, the same basic shape is kept, only now conduction takes place more rapidly with time (see fig. 18); also note the increased conductivity at the oxidation and reduction ends of the voltammogram i.e fig. 18 and 19. Also note the small oxidation wave at about +.32V not seen either in PR or TBO.

In poly(CH)-TBO, there is a similarity to the cyclic of the PR polymer, only now there is a slight change in the slope of the reduction wave and a lessening in the intensity of the oxidation wave. However, the basic similarity of the two CV's is supportive of the formation of a conjugated and thereby conductive, backbone in these polymers.

It is clear that the enhanced conductivity of the two polymer coated electrodes at +1.15V and -.58V show that

the polymer is indeed able to sustain the water oxidation and reduction processes and, in fact, make them somewhat easier to accomplish. Thus both the oxidative and reductive waves are more intense than for the naked Pt electrode.

Moreover, since the conductivity increases with time, each electrochemical sweep appears to make the layer more conductive than the previous one, so that the polymer is not losing its conductive qualities due to it being attacked by intermediates present in the water electrolysis.

It should be noted that the processes which are the sources of the waves have not been strictly identified, and they may be irreversible redox reactions of the polymer itself and not water. However, if this were the case, a successively more insulating polymer would be expected, contrary to what is observed.

Thus, it appears that the polymer coating is able to electrochemically catalyze water redox reactions and to retain its integrity in so doing. It remains to be seen if there is any photoactivity discernable.

Figure 16: Cyclic Voltammograms of permollic acid and the supporting electrolyte Na_2SO_4 .

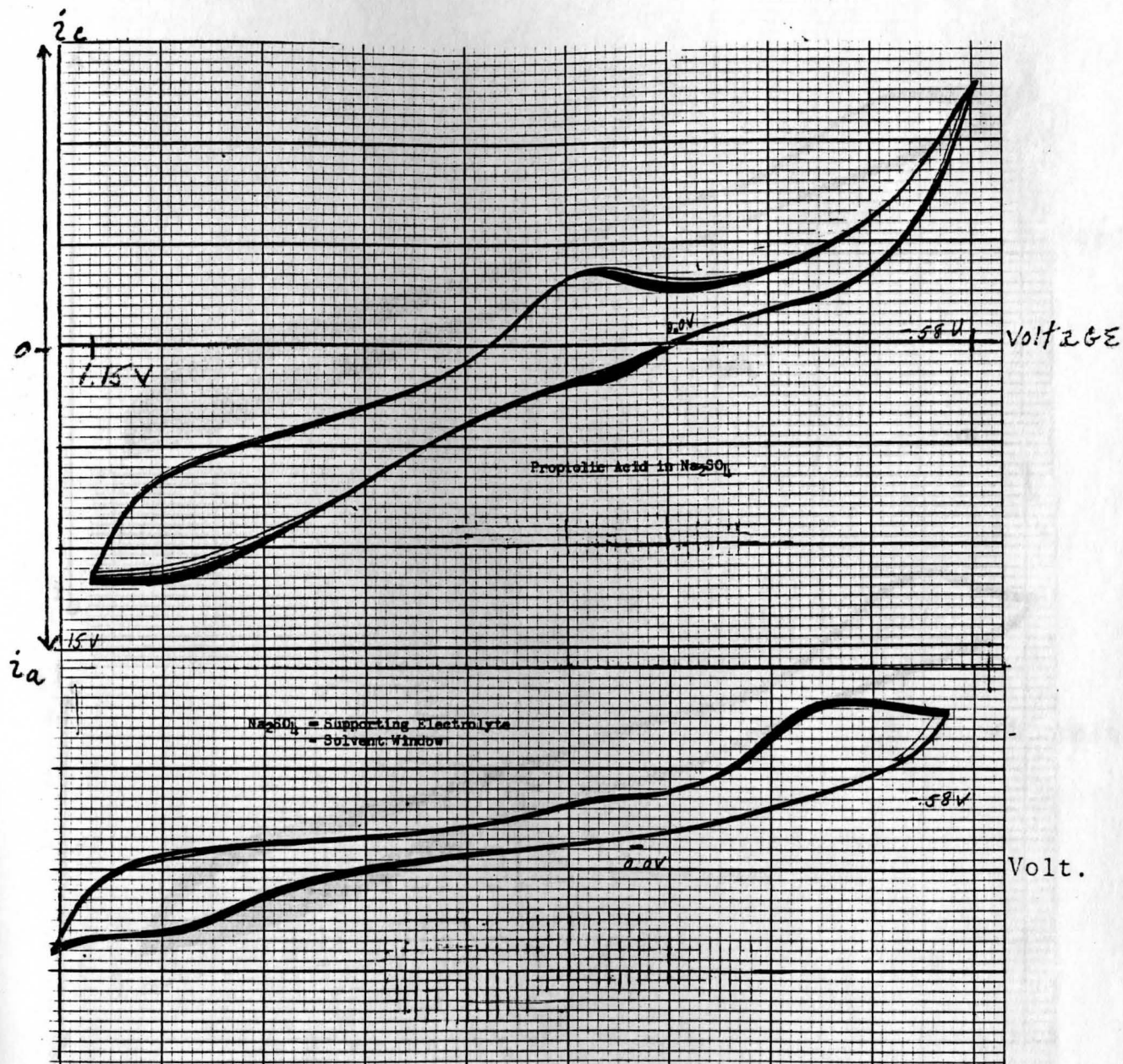


Figure 16: Cyclic Voltammograms of propionic acid and the supporting electrolyte Na_2SO_4 .

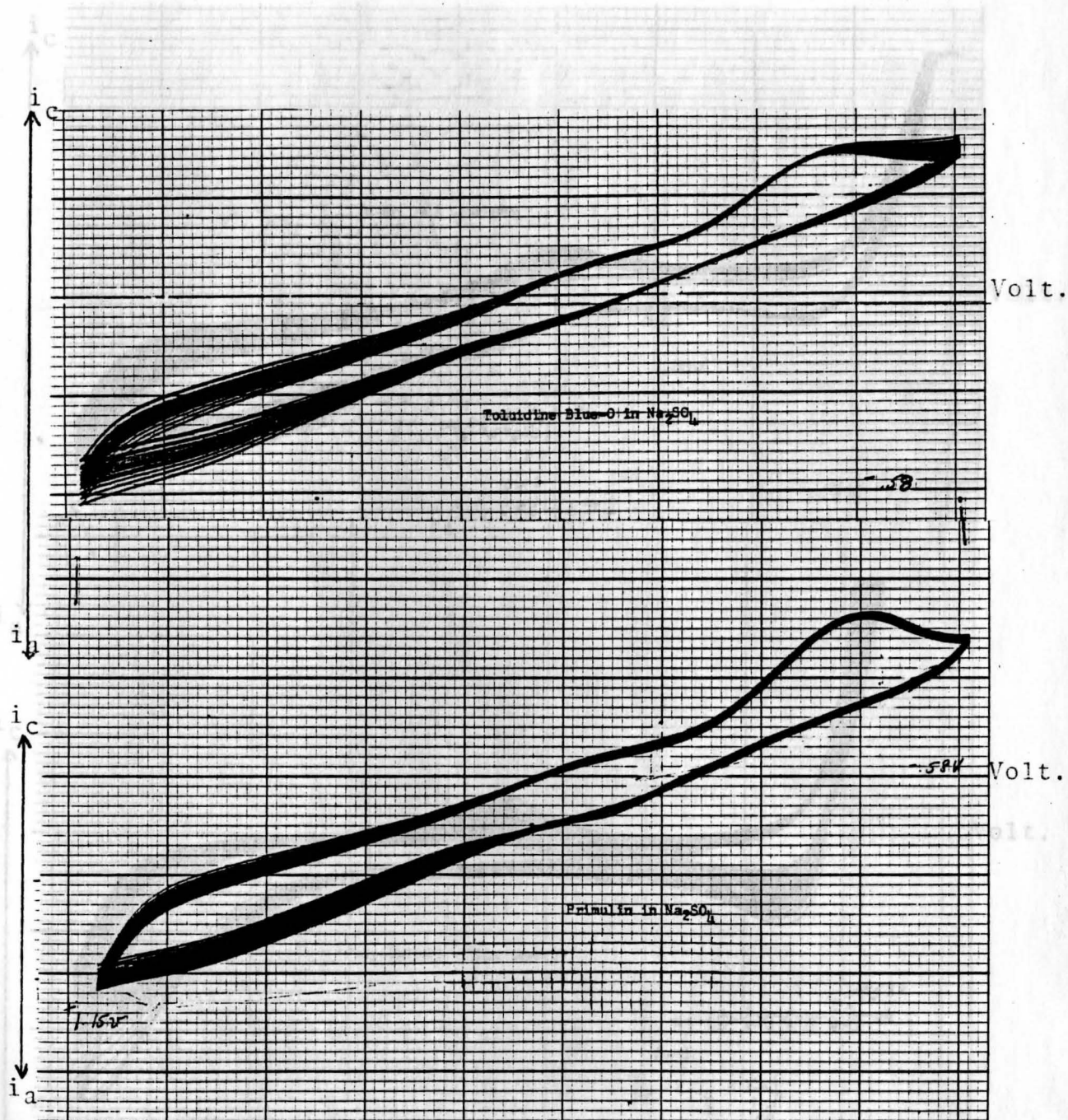


Figure 17: Control CV's of the dyes TBO and PR.

Figure 18 Cyclic voltammograms of poly(OH)-TBO and poly(OH)-PR.
30 minute CV time.

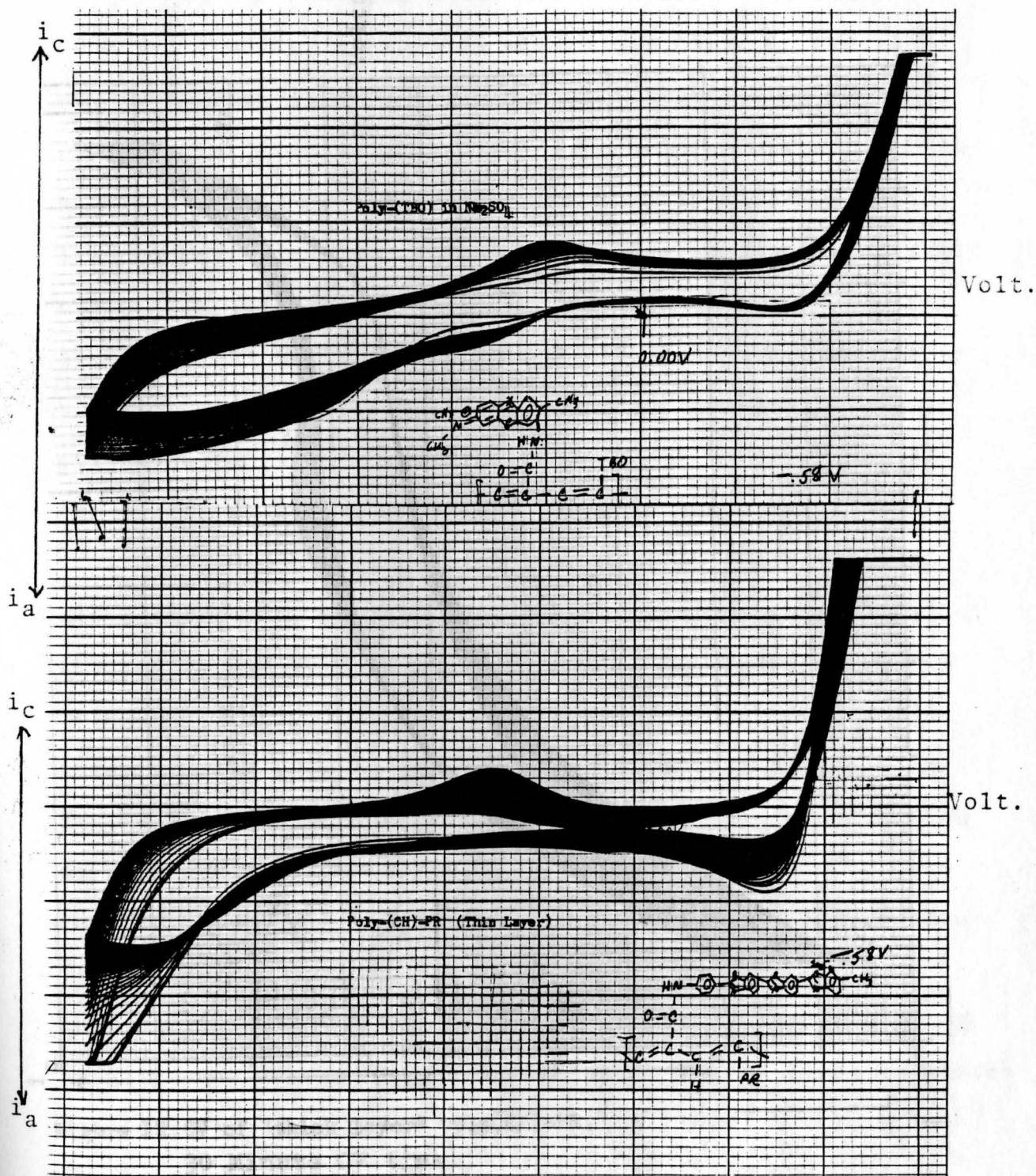


Figure 18 Cyclic voltammograms of poly(CH)-TBO and poly(CH)-PR.
30 minute CV time.

Photoelectrochemistry of Poly(CH)-Dyes

It has not been until very recently that significant solar energy conversion efficiency could be realized

Voltage

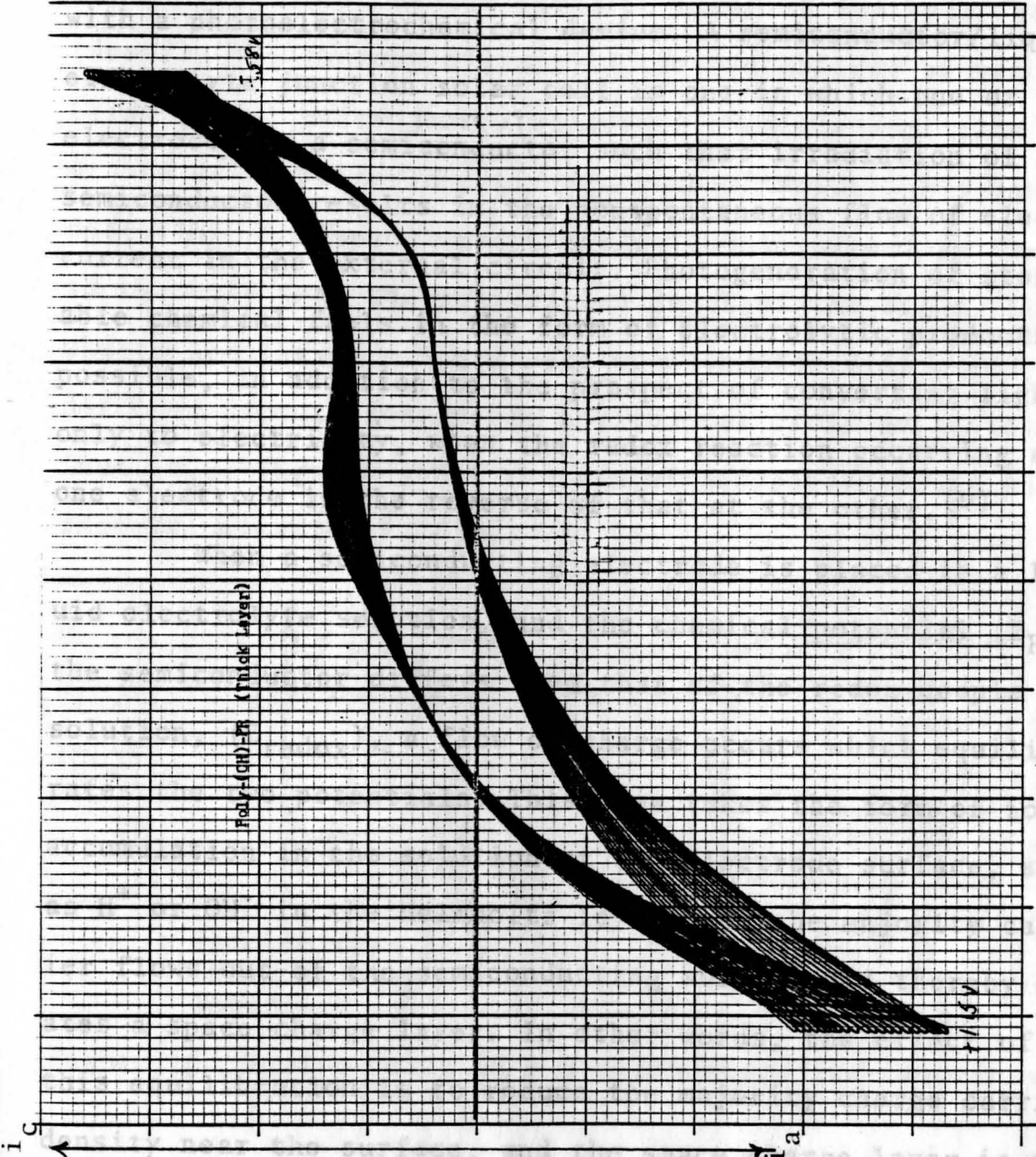


Figure 19 CV of "thick layer" poly(CH)-PR. 30 Minute CV time.

al electric field results from this flow, and the valence and conduction bands bend as in fig.20, for typical n- and p-type semiconductors. A high barrier exists which prevents

further a Photoelectrochemistry of Poly(CH)-Dyes

If such a semiconductor is illuminated at its surface, $h\nu/e^-$ pairs are generated in the depletion layer. They may be separated by the electric field at the interface with a photoelectrochemical device. A semiconductor/liquid electrolyte junction solar cell is one in which one or both electrodes is a semiconductor such that irradiation of the semiconductor results in the nonspontaneous flow of electric current in the external circuit. Photogeneration of storable chemical fuels in the form of electrolytic products is possible, in addition to the prospect of converting light only to electricity, when the redox reaction occurring at one electrode is the reverse of that at the other. (6)

When a semiconducting electrode is placed in a liquid electrolyte solution, and the chemical potential (E_F) of the semiconductor differs from that of the redox couple in solution, (E_{redox}), a flow of charge occurs which equilibrates the two potentials. This flow takes the form of ion accumulation in the solution at the electrode surface, such as H^+ or OH^- in the Helmholtz layer, and the majority carrier flows out of the semiconducting surface and thereby creates a space charge layer. In other words, the effect of this equilibration is to reduce the majority charge carrier density near the surface, and the space charge layer is therefore also referred to as the depletion layer. A strong local electric field results from this flow, and the valence and conduction bands bend as in fig.20, for typical n- and p-type semiconductors. A high barrier exists which prevents

further e^- flow into the electrolyte. If such a semiconductor is illuminated at its surface, h^+/e^- pairs are generated in the depletion layer. They may be separated by the electric field at the interface (see fig.20) thereby minimizing the probability of recombination (h^+/e^- pairs generated deeper than the depletion layer are essentially lost through recombination). For optimal operation, the space charge region should extend further into the bulk than the penetration depth of the light. This charge separation process sets up a counter field, and, under open circuit conditions the counter field is at its maximum, V_{OC} . Figure 20 shows the diminished band bending under photoillumination.

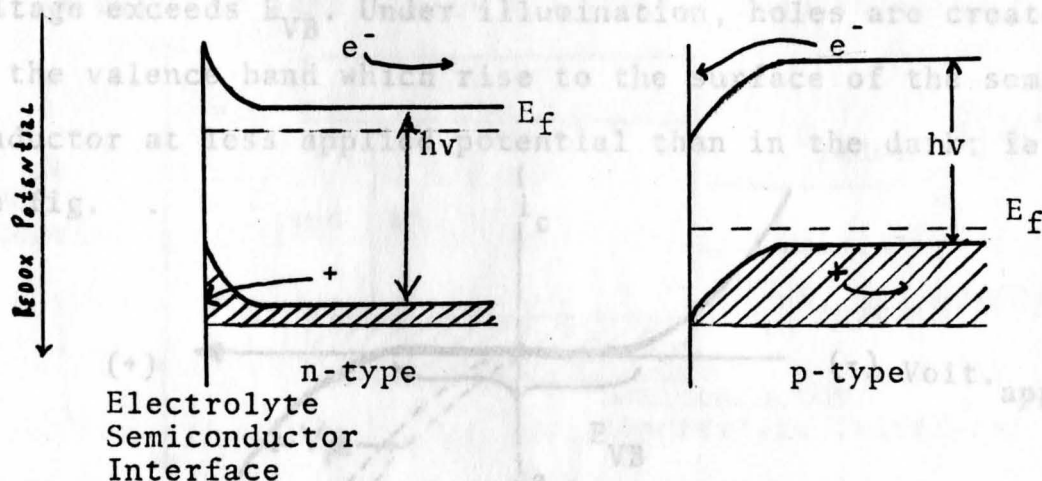


Figure 20: Band bending in a semiconductor immersed in an electrolyte solution.

During illumination a counter field is created which shifts the valence and conduction bands up. The photovoltage is the change in the Fermi levels. E_c' and E_v' are the conduction and valence bands under illumination. If a count-

er electrode is immersed in the same solution, the photovoltage can drive a current which can then perform electrolysis. This photovoltage is merely the difference between the E_F 's before and after illumination.

In the present work, the electrochemical behavior of the electrodes is characterized by current-voltage plots, called voltammograms which are measured on an x-y recorder. A typical current-voltage plot for an n-type semiconductor is shown in the following figure. By applying a negative potential to the semiconductor, the valence, conduction and Fermi levels are all raised until the barrier at the interface is surmounted and reduction begins. When the applied voltage is swept positively, no current will flow until the voltage exceeds E_{VB} . Under illumination, holes are created in the valence band which rise to the surface of the semiconductor at less applied potential than in the dark; i.e.

see fig.

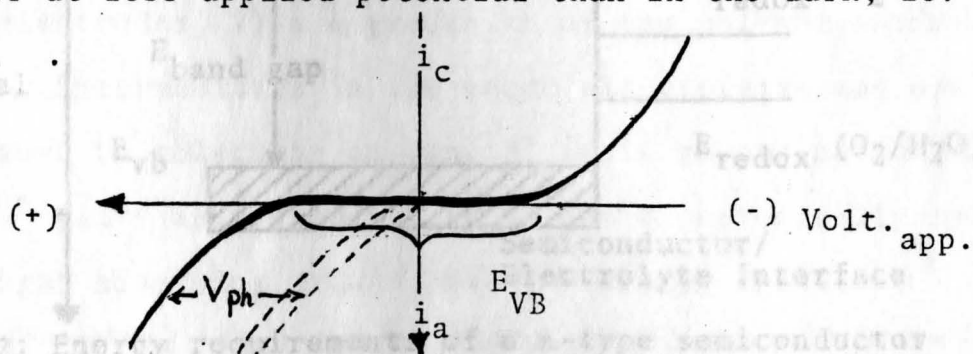


Figure 21: The current-voltage plot for an n-type semiconductor in the dark (—) and in the light (---).

Since the goal of this work is to cleave H_2O into both its components H_2 and O_2 , simultaneous oxidation (at the n-type surface) and reduction (at the p-type surface) are required. A violet light source manufactured by the Hanovia Lamp Divis-

need to be considered. The relevant reactions are:

			Redox Pot (V vs SCE)
Anode	$2h^+ + H_2O$	$1/2 O_2 + 2H^+$	n-type .57
Cathode	$2e^- + 2H^+$	H_2	p-type -.66
Net	H_2O	$1/2 O_2 + H_2$	

The thermodynamic requirements necessary to split water are that the Fermi levels of the semiconductor must differ by at least the decomposition voltage (1.23V) of H_2O , that the valence band of the n-type semiconductor be more positive than the O_2/H_2O couple, and that the conduction band of the p-type semiconductor be more negative than the H^+/H_2 couple. (Strictly speaking, the approximate energies are given by the respective Fermi levels for the e^- and the h^+ , so that the band levels are minimal requirements), i.e.

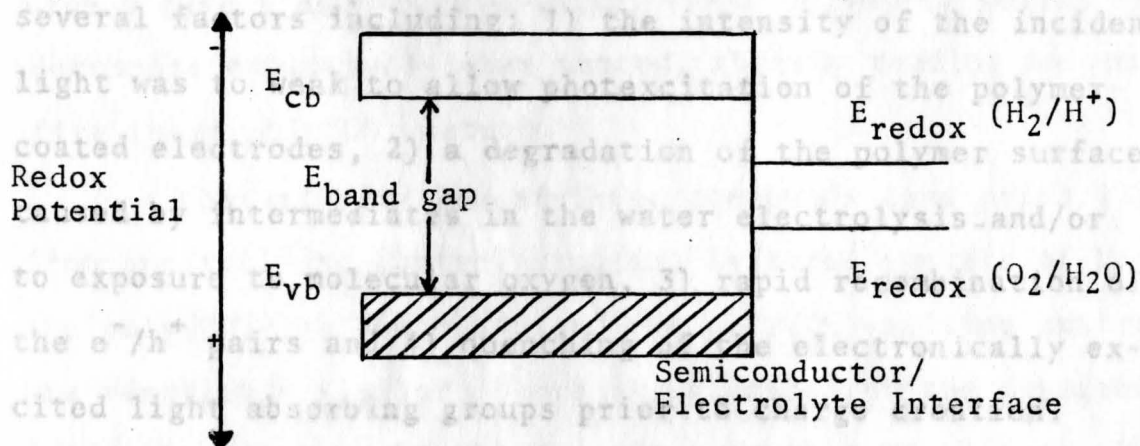


Figure 22: Energy requirements of a n-type semiconductor to photochemically oxidize and reduce H_2O .

Experimental-Polymer Photoelectrochemistry

The apparatus used in addition to that described for the cyclic voltammetry setup included a 1000 watt ultraviolet light source manufactured by the Hanovia Lamp Divis-

ion and tuned by a Jarrel-Ash monochromator. This experiment was the same as that detailed for cyclic voltammetry, only now the coated electrode is additionally photoilluminated and the current monitored. The light frequencies selected were those of the mercury lines of wavelengths 5770, 5461, 4358 and 4047 Å. These are the most intense illuminating frequencies as they are the Hg atomic spectral lines of the mercury vapor light source.

The only light reaction noted with these polymerically coated electrodes was a very slight enhancement of the reduction wave. Obviously, the light is enhancing the reduction of the poly(CH)-Dye materials.

The observed lack of photovoltage could be due to several factors including: 1) the intensity of the incident light was too weak to allow photexcitation of the polymer coated electrodes, 2) a degradation of the polymer surface caused by intermediates in the water electrolysis and/or to exposure to molecular oxygen, 3) rapid recombination of the e^-/h^+ pairs and 4) quenching of the electronically excited light absorbing groups prior to charge creation.

However, the observed photoenhancement of the reductive conductivity could be due to the simple creation of more charge carriers in the light, as normal p-type materials are ideally blocking to reductions in the dark. If this is so, then some separation of the e^-/h^+ is occurring.

CHAPTER V

CONCLUSIONS

The synthesis of a semiconductive polymer which is both stable under the conditions of water photoelectrolysis and able to undergo repeated redox reactions has not been attempted until now. We have taken organic ionic dyes and attached them via an amide linkage to a polyacetylene semiconducting backbone, whose precursor is propiolic acid. For each of the dyes, a crystalline solid was obtained from the polymerization reaction. The anionic dye Primulin gave a deep reddish-brown crystal, while the cationic dye Toluidine Blue-0 gave a deep purple solid. These polymeric solids do decompose explosively when heated, thereby tending to confirm their poly(CH) nature.

Characterization of these compounds came primarily from spectral and control studies. Infrared spectra of both the poly(CH)-dye compounds and the poly(CH)-aniline control are remarkably similar. There is evidence for the expected amide linkage and all three spectra exhibit an intense absorption at the high frequency portion of the spectrum due to the -NH stretching function, and also to a strong "black-body" absorption observed for both doped and undoped polyacetylenes by Kleist and Byrd. (10)

NMR experiments were used both for purposes of polymer characterization and kinetic studies of the polymer

formation. These spectra demonstrated the large broadening of the acetylenic resonance with time, similar to NMR spectra of polyacetylene done by Green et.al.,⁽²¹⁾ and also the shifting and intensity decrease of the amine absorption of the dyes indicating the synthesis of the amide -NH from the amine -NH₂. Loss of the free acid -OH is seen in most of these spectra.

Physical measurements included a test of the magnetic susceptibility of the polymers and characterization of their electrochemical properties utilizing cyclic voltammetry. The poly(CH)-PR compound was found to be paramagnetic, while the poly(CH)-TBO was nonmagnetic. Paramagnetism is observed in poly(CH) due to the presence of unpaired e⁻, or solitons, as detailed in work by Chien. This is a direct piece of evidence which points to the formation of a poly-(CH) backbone. Cyclic voltammetric experiments indicated that both polymers are electroactive and this activity is similar for both compounds. Each showed an ability to increase the reduction and oxidation waves of the Na₂SO₄-H₂O solvent window along with the appearance of new redox waves for each.

When these polymerically coated platinum electrodes were exposed to ultraviolet light, only slight photoenhancement was observed. Several conditions could be responsible for this effect including poly(CH)-dye susceptibility to atmospheric oxygen degradation,⁽¹⁴⁾ polymer surface decomposition, as noted by the film flaking off the electrode, due to

since a slight enhancement of the reductive current occurs on illumination, e^-/h^+ pairs are at least partially separated within the polymer.

Earlier experiments have mainly combined electroactive polymer films with known, small band gap semiconductors and have demonstrated the feasibility of using such systems in the photoelectrochemical decomposition of water. Both gaseous H_2 and O_2 have been separately generated from polymer coated photoelectrodes: H_2 from poly-methyl-violgen⁺² on p-Si and O_2 from polypyrrole films on n-CdS. Our goal was to combine the functions of light absorption, charge creation and separation, followed by catalytic transformation of chemical potential into new products, all into a single polymeric device. Our experiments realized the synthesis of a polymer, which contained the light absorbing and charge carrying units, and which also demonstrated electrocatalytic activity and weak photoelectrochemical catalytic activity.

Further work, which may boost the observed photoenhancement, involves adjusting the amount of covalently bound dopant (the dye material) incorporated into the polymer. This would then allow adjustment of the depletion layer of the n-type polymeric material according to the following relation:

$$W = (2\epsilon\epsilon_0 V_B / qN)^{1/2} \quad (28)$$

where V_B is the amount of band bending in the depletion layer, q is the electronic charge, ϵ is the dielectric constant of the semiconductor, ϵ_0 is the permittivity of free

REFERENCES

- space, and W =the width of the depletion layer present in the semiconductor. ⁽²⁴⁾ Therefore, this adjustment of the depletion layer is directly regulated by the amount of holes added to the semiconducting material i.e. which should be proportional to the amount of dye which is bound to the poly(CH) backbone. It remains to be seen if the photoenhancement can, indeed, be increased by this adjustment.
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