

SYNTHESIS OF ELECTRICALLY CONDUCTIVE  
POLYPYRROLE THIN FILMS  
VIA AMMONIUM PERSULFATE CHEMISTRY

by

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Submitted to the Department of Materials Science and Engineering  
on May 11, 1990 in partial fulfillment of the requirements for  
the Degree of Bachelor of Science in  
Materials Science and Engineering

ABSTRACT

The feasibility of using ammonium persulfate in the production of conductive polypyrrole Langmuir-Blodgett thin films was investigated. Three bulk films were synthesized; one in ferric chloride, the second in ammonium persulfate and 1M HCl, and the third in ammonium persulfate and water. Conductivity measurements of the films indicated that a subphase consisting of ammonium persulfate, on the order of 0.5 wt%, in 1M HCl produced a material of comparable quality to that made using the usual 1 wt% ferric chloride. The use of persulfate without HCl resulted in a poorer film. Experiments conducted on an LB film balance demonstrated that a spreading solution of 2000:1:1 (moles of pyrrole:moles of 3ODOP:ml of chloroform/mg of 3ODOP) was most effective in conjunction with an oxidizer concentration of 0.2 wt%. Observations used to evaluate the films were the lack of excess pyrrole formation in the trough, successful spreading of the monomer, and FTIR studies. Characterization and full evaluation of the newly produced material has not yet been performed.

Thesis Supervisor: Prof. Michael F. Rubner

Title: Associate Professor of Polymer Physics

## TABLE OF CONTENTS

1.0	Introduction	p. 7
2.0	Background	8
2.1	Langmuir-Blodgett Thin Film Processing Technique	8
2.2	Polypyrrole Production - Current Chemistry	14
3.0	Experimental Procedures	20
3.1	Proposed Chemistry	20
3.2	Bulk Film Production	20
3.3	Conductivity and Stability Measurements	21
3.4	Monolayer Chemistry	22
3.5	Infrared and Optical Absorption	23
4.0	Results and Discussion	24
4.1	Bulk Films: PPY-2 vs PPY-1	24
4.1.1	General Observations	24
4.1.2	Fourier Transform Infrared Spectroscopy	25
4.1.3	Optical Properties	26
4.1.4	Conductivity	27
4.1.5	Stability	28
4.2	PPY-2 Monolayer Chemistry	29
4.2.1	General Observations	30
4.2.2	Isotherms	33
4.2.3	Fourier Transform Infrared Spectroscopy	35
5.0	Conclusions and Recommendations	39
6.0	Appendix	40
7.0	References and Notes	41

## LIST OF FIGURES

Figure 1:	Electron Delocalization in a Conjugated Polymer	p. 7
Figure 2:	Langmuir-Blodgett Film Balance	10
Figure 3:	Gas, Liquid, and Solid Phases of a Monolayer as Represented by a Pressure-Area Isotherm	11
Figure 4:	Y-Type Dipping	13
Figure 5:	Polypyrrole (a) Polymerization and (b) Doping	16
Figure 6:	3-Octadecanoyl Pyrrole	17
Figure 7:	Alteration of the LB Trough to Accommodate Washing	19
Figure 8:	Four-Point Probe Arrangement	22
Figure 9:	FTIR Spectrum of Polypyrrole Showing Key Peaks	25
Figure 10:	FTIR Spectrum of Bulk PPY-2	26
Figure 11:	Optical Spectra of Bulk PPY; (A) PPY-1, (B) PPY-2/HCl, and (C) PPY-2/Water	27
Figure 12:	Conductivity vs. Time	28
Figure 13:	Isotherms of Samples 4,5,10,13, and 16	34
Figure 14:	Reported FTIR Spectra of 3ODOP, P/3ODOP (5000:1), and Bulk PPY	34
Figure 15:	Effect of Parameter Variation on PPY Content of Films Made on the LB Trough	37
Figure 16:	FTIR Spectra of Real and Supposed 2000:1:1 Sample Solutions	38

## LIST OF TABLES

Table 1:	Possible Applications for LB Thin Films of Electroactive Polymers	.....page9
Table 2:	Materials Used in LB Research	.....15
Table 3:	LB Conditions for the Production of Polypyrrole Using Ferric Chloride	.....18
Table 4:	Pyrrrole Polymerization Experiments on the LB Film Balance	.....31

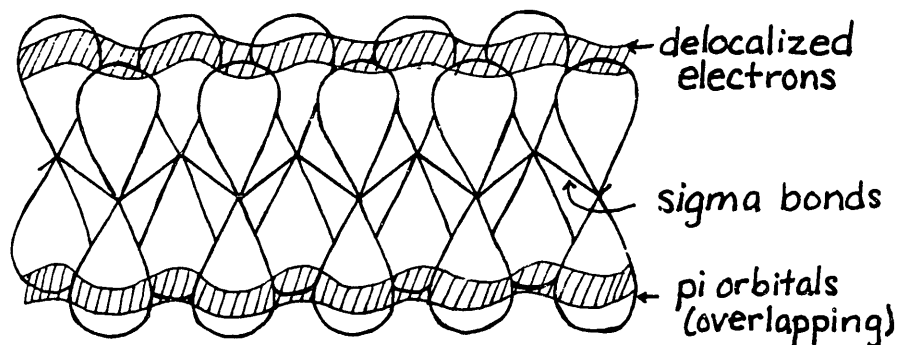
## **ACKNOWLEDGEMENTS**

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## 1.0 Introduction

During the past few decades, recognition of the versatility of polymers has resulted in the invasion of many materials applications previously reserved for metals. One of the more recent areas of investigation for polymers has been that of electronics/optics, which has required the production and evaluation of electroactive polymers. Finding a successful, practical method for manipulation of these materials into the desired form while retaining optimum properties has been the focus of much of this research. Most experiments have been directly concerned with the production of high quality conductive films using a variety of electroactive polymers.

Electroactivity in polymers is realized by delocalization of electrons along the backbone of a conjugated polymer chain, as depicted in Figure 1. When the chains are fully aligned, the system becomes one-dimensional, resulting in highly anisotropic electrical and optical properties. The electronic state of the delocalized backbone, which directly influences these properties, is, itself, affected by side groups that exist along the chain. For instance, the presence of strong electron donating or accepting groups can alter the delocalization of electrons along the backbone. Another important characteristic of these electroactive materials is that they are highly susceptible to oxidation and reduction and can, therefore, be doped into a conducting state; an extremely useful phenomenon if this state is stable enough to be maintained over a given period of time.



**FIGURE 1: ELECTRON DELOCALIZATION IN A CONJUGATED POLYMER**

Thin film production of electroactive polymers, especially those that are in their conducting states, is an area of rather high activity due to the many possible uses for such materials [1,2], (see Table 1). Unfortunately, the films required to fulfill these needs must be extremely well-ordered and have an accurately known thickness. Providing films of a high enough degree of structural perfection has proved to be quite difficult. The most recent investigations have centered upon the Langmuir-Blodgett (LB) thin film processing technique; at present, the most feasible method.

## **2.0 BACKGROUND**

### **2.1 LANGMUIR-BLODGETT THIN FILM PROCESSING TECHNIQUE**

The LB technique is based upon the formation of a layer of material only one molecule thick at a liquid-gas interface. The material used must be amphiphilic, containing a hydrophilic head group and a hydrophobic tail group [3]. This property allows the molecule to float at the liquid surface; the head group attempts to submerge and dissipate into the solution, but the tail groups are so repelled by the polar subphase that they keep the molecule suspended at the interface. To facilitate complete spreading across the entire surface, the material is diluted in a highly surface-active solvent which evaporates quickly after deposition onto the subphase.

This film formation process is performed at constant temperature on an LB film balance, or "trough," pictured in Figure 2. After the material of interest has been deposited onto the subphase, it disperses across the surface while the solvent evaporates. The film is then compressed by means of a movable barrier to effect a two-dimensional solid state whose presence is indicated on an isothermal plot of pressure (differential surface tension),  $P$ , vs area per molecule of the film,  $A$ .

Similar to three-dimensional systems, the 2-D monomolecular film exists in three primary states; gaseous, liquid, and solid. Each is characterized by a different slope in the  $P$ - $A$  isotherm, although the liquid phase is often composed of two substates, and two-phase regions are sometimes exhibited. In the gaseous state, no molecular interaction occurs; the liquid state involves interaction of the tails



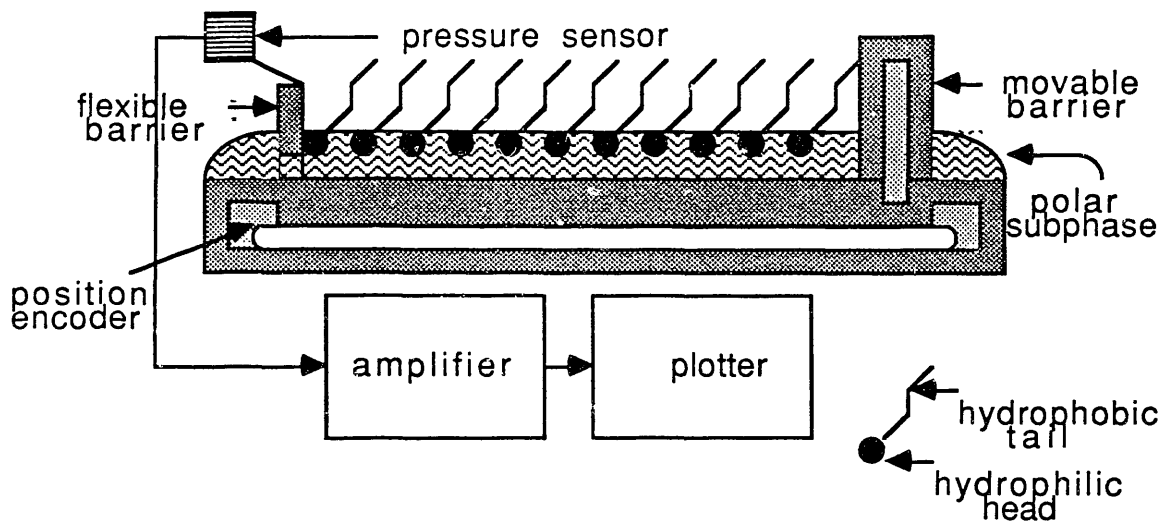
**TABLE 1: POSSIBLE APPLICATIONS FOR LB THIN FILMS  
OF ELECTROACTIVE POLYMERS**

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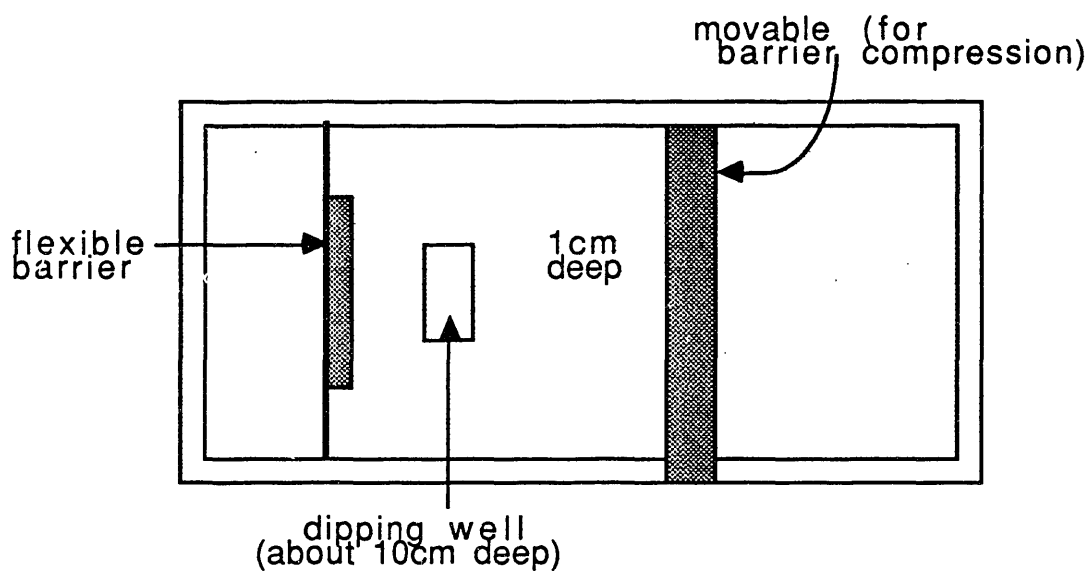
- two dimensional electronic transport
- tunneling behavior
- nonlinear optical behavior
- electroluminescence

**APPLICATIONS:**

- optical frequency conversion,  
switching, and modulation
- planar waveguides
- optical rectifiers
- high capacity capacitors
- chemical sensors
- memory devices
- transistors
- electron beam resists



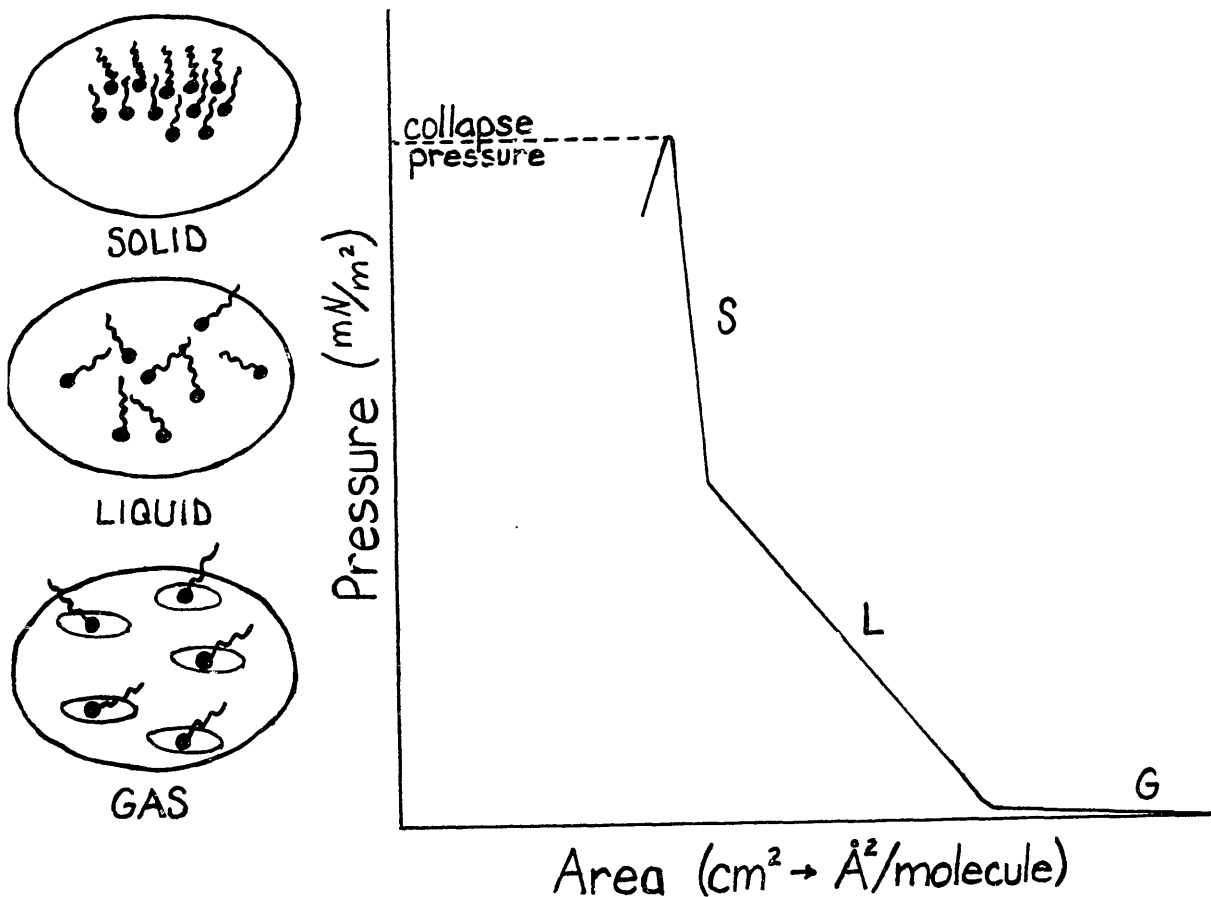
(A) SIDE VIEW



(B) TOP VIEW

FIGURE 2: LANGMUIR-BLODGETT FILM BALANCE

of neighboring molecules and limited compressibility; and the solid state is characterized by closer-packed molecules oriented perpendicular to the surface. The latter is usually left to anneal for a period of time to achieve the maximum close packing. Figure 3 depicts the monolayer in each of these states and shows a sample isotherm that would be associated with the system. In addition to indicating when the film is in its solid state, the isotherm can also be a good indicator of purity. Any foreign materials present in the system will usually result in a change in the usual position or slope of the isotherm.

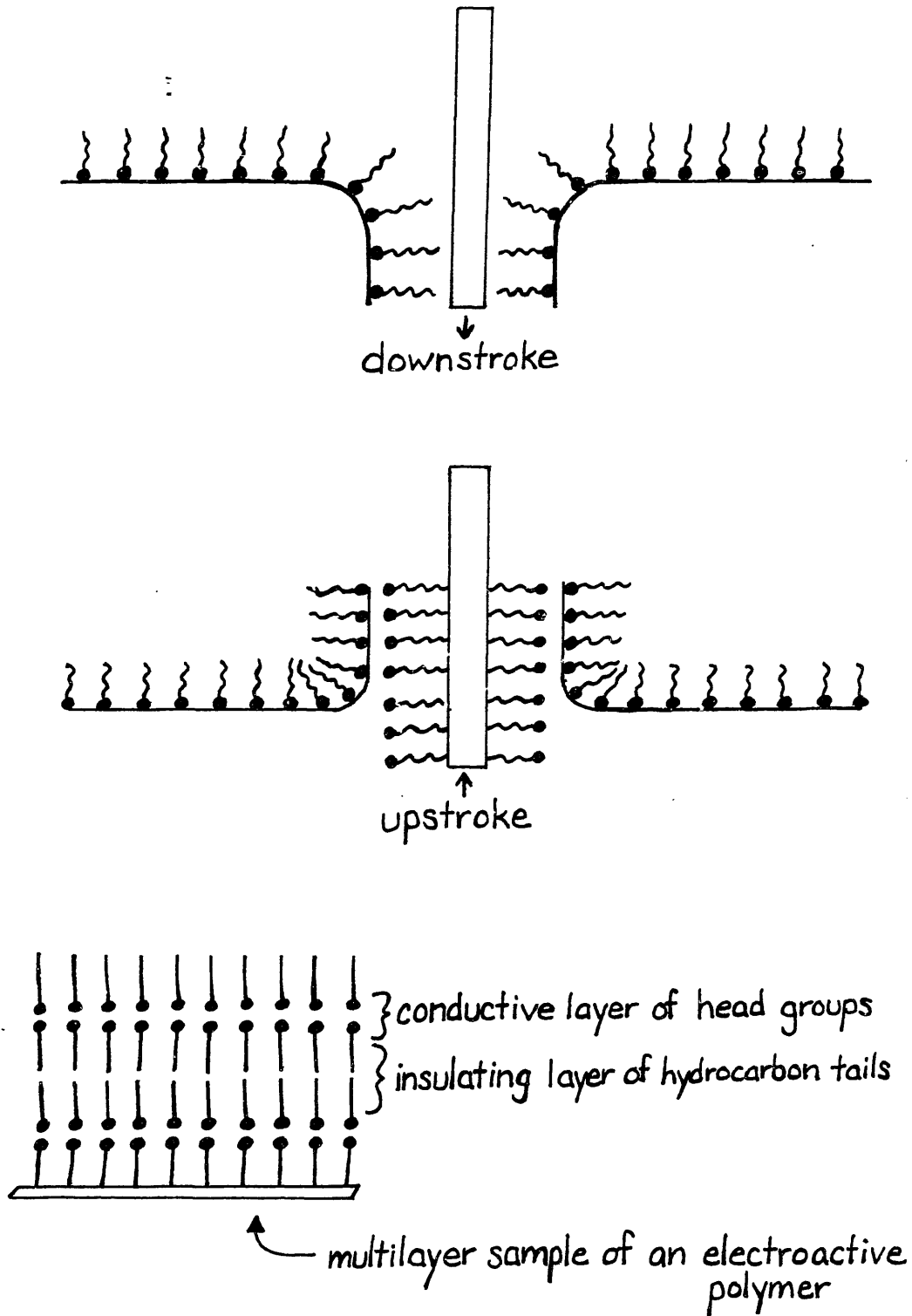


**FIGURE 3: GAS, LIQUID, AND SOLID PHASES OF A MONOLAYER AS REPRESENTED BY A PRESSURE-AREA ISOTHERM**

Monitoring the pressure and area/molecule becomes extremely important during the fabrication of multilayer films. Deposition onto a specific substrate (usually some kind of glass slide) is achieved by a vertical dipping method. To ensure adhesion of the film to the substrate, the slide is most often pre-treated to render it either hydrophobic or hydrophilic. The slide is then positioned perpendicular to the film and is slowly lowered in to a desired depth, held at its lowest point for a short time, then raised up out of the film again. This process is subsequently repeated so as to develop a multilayer film by depositing monolayers one at a time on top of each other. Constant pressure is maintained during this process to further encourage deposition and to keep the material in its quasi-solid state. As film is deposited, the area must decrease in order to sustain this pressure, so the amount of the material deposited can be calculated. (An increase in area is indicative of the loss of material from the slide into the subphase).

A number of supermolecular structures may be produced using the vertical dipping method, but the one most amenable to 2-D electronic transport is the "Y-type," [3], pictured in Figure 4. As the substrate is dipped, the flexible film is gradually depressed and forced down into the subphase. The film's hydrophobic tails are attracted to the hydrophobic slide, and the pressure exerted by the movable barrier provides additional force to aid in the attachment. When the slide has reached its deepest point, it is stopped for about thirty seconds to allow the film to settle. The slide is then slowly retracted. Head groups will now adhere to the other head groups which protrude from the substrate. If an electroactive polymer is used and is first oxidized, multiple dips will result in a structure that consists of layers of conducting head groups separated by layers of insulating tail groups: a highly ordered, two-dimensional conductive polymer of accurately known thickness. An added benefit is that this whole procedure is carried out at a much lower temperature than other deposition processes such as sputtering, evaporation, or growth from a plasma.

A list of the most commonly used materials for this process



**FIGURE 4: Y-TYPE DIPPING**

can be found in Table 2. Again, electroactive polymers are the materials of interest. Their ability to easily form films, as well as their good mechanical and thermal properties as compared to those of fatty acids [1,4], allows them to be successful candidates for LB processing. Of the materials listed, polypyrrole is one that has encountered a great deal of success. Its stability in air and its electrical properties are promising for future use in various device applications, [5]. Well-oriented LB films of high reproducibility have been made and characterized [7], and the quality of such properties as capacitance and in-plane conductivity has warranted further investigation of thin films of this material.



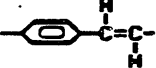



## **2.2 POLYPYRROLE PRODUCTION - CURRENT CHEMISTRY**

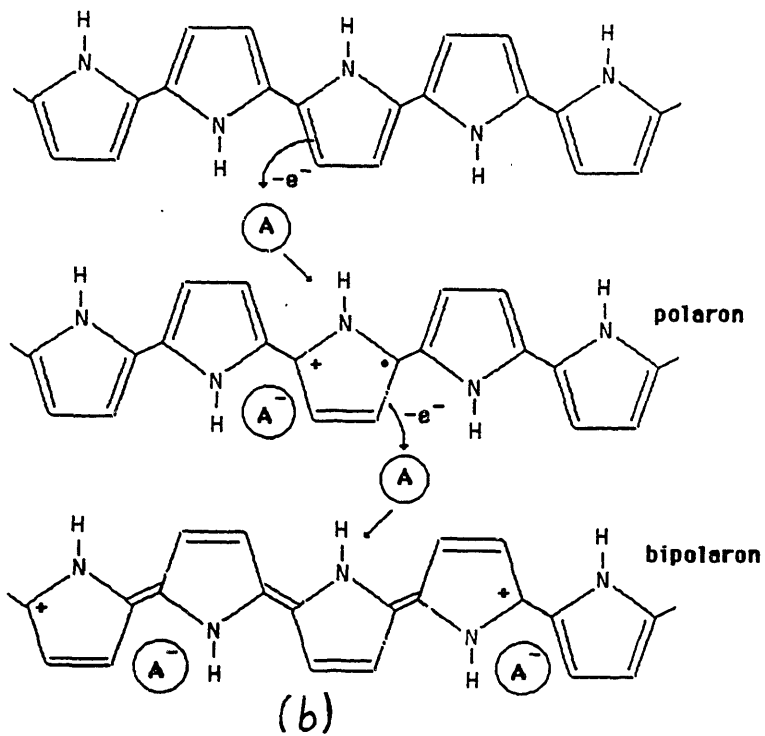
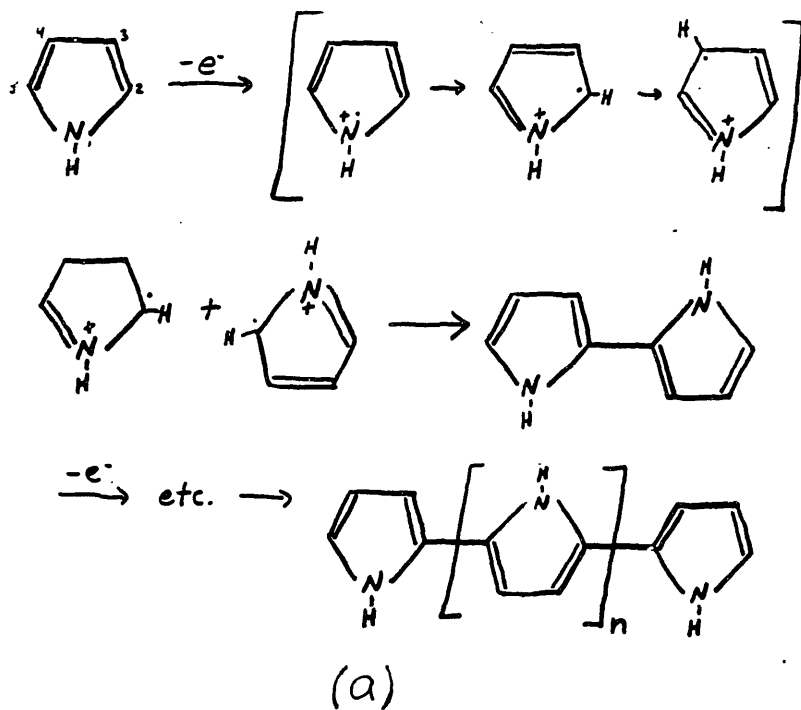
Pyrrrole is a five-membered heterocycle which polymerizes via the 2,5 positions [6] as shown in Figure 5a. A radical cation mechanism is initiated in the presence of a strong oxidizing agent which also serves as the dopant. Bipolarons result via the mechanism shown in Figure 5b, rendering the polymer electrically conductive. In accordance with the general LB method, the procedure for making conductive polypyrrole thin films would be to deposit the polymer directly onto a water subphase.

Since directly administering a layer of polymer onto the surface of the subphase would be a difficult task, a possible alternative for polypyrrole is deposition of the monomer onto a subphase containing the necessary initiator. The monomer, theoretically, would polymerize at the surface and subsequently become electrochemically doped. For polypyrrole, however, the chemistry is much more involved, [7].

The first problem is the fact that pyrrole monomer is not surface-active, as required for LB processing. It readily dissolves in water and, therefore, will not stay at the interface. Common spreading solutions do not alleviate this problem, so substituted pyrrole monomers were developed. A long hydrophobic chain, or tail, is added to the pyrrole ring to render it surface-active. Since polymerization proceeds via the 2,5 members, 3-substituted

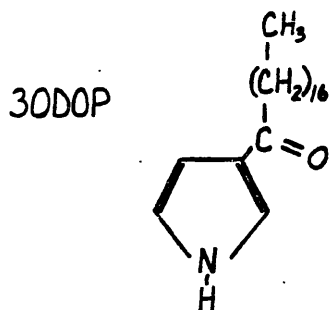
**TABLE 2: MATERIALS USED IN LB RESEARCH**

Polymer	Conductivity ( $\Omega^{-1}\text{cm}^{-1}$ )	Stability (doped state)	Processing Possibilities
Polyacetylene $\begin{array}{c} \text{H} \\   \\ -\text{C}=\text{C}- \\   \\ \text{H} \end{array}$	$10^3 - 10^5$	poor	limited
Polyphenylene 	1000	poor	limited
PPS 	100	poor	excellent
PPV 	1000	poor	limited
Polypyrroles 	100	good	good
Polythiophenes 	100	good	excellent
Polyaniline 	10	good	good



**FIGURE 5: POLYPYRROLE (a) POLYMERIZATION AND (b) DOPING**





**FIGURE 6: 3-OCTADECANOYL PYRROLE**

pyrroles were created. 3-octadecanoyl pyrrole (3ODOP) is the one that is now used, (see Figure 6 for its structure).

The second problem is that this surface-active material does not readily polymerize; the result of three effects: (1) the carbonyl is an electron withdrawing group so it significantly deactivates the ring to subsequent polymerization, (2) polymerization can only occur at the sacrifice of tail arrangement, and (3) steric effects; the molecules cannot easily get close enough to facilitate polymerization. As a result, a mixture of 3ODOP and pyrrole monomers is now used, along with chloroform to further enhance spreading. A large excess of pyrrole (mole ratio of 5000:1) is required since much of the monomer will dissolve in the subphase while only a small percentage will be sufficiently attracted to the 3ODOP surface layer. Theoretically, van der Waals forces allow the polypyrrole to adsorb underneath the 3ODOP although, experimentally, it appears to enter the monolayer also. The former situation is most desirable and would consist of a layer of 3ODOP monomer at the surface with a layer of uninterrupted conductive polypyrrole directly beneath it; a better oriented and more predictable system than the latter.

Present conditions for the production of these films [7] still leave room for improvement. The well-established method which has seen significant activity uses ferric chloride as both the polymerization and doping agent. (Experimental conditions are listed in Table 3). Unfortunately, this material is extremely corrosive and slowly eats away at the teflon coating on the trough.

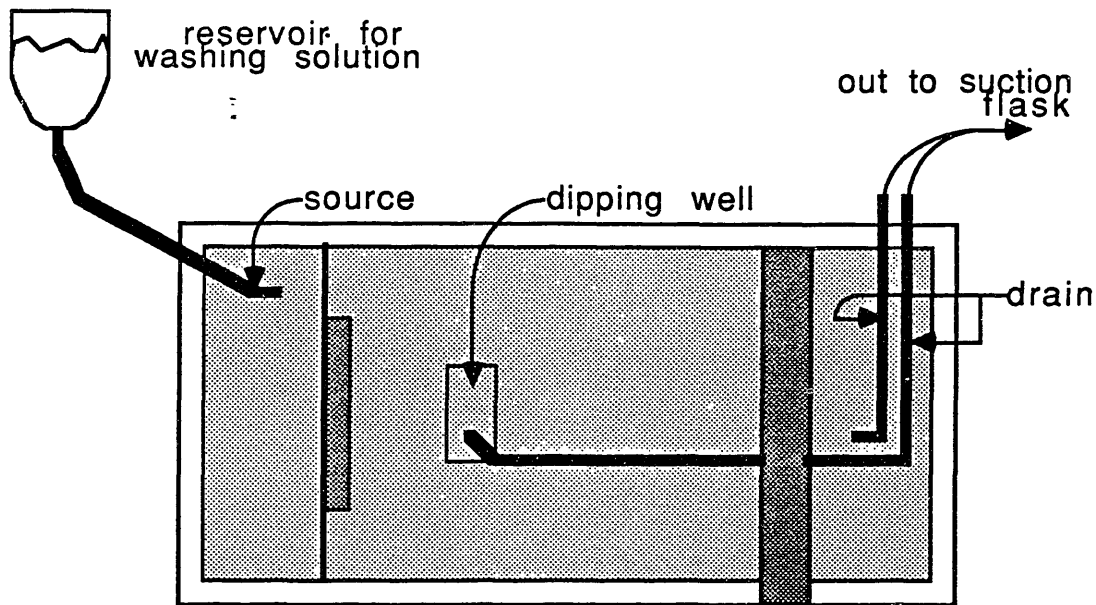
**TABLE 3: LB CONDITIONS FOR THE PRODUCTION OF POLYPYRROLE USING FECL3 CHEMISTRY**

Spreading solution	[FECL3]	Reaction time	Washes
5000:1:1 (pyrrole:3ODOP:CHCL3)	1%	5 min*	2L HCl 3L water

\*5 minutes is the amount of time required to compress the film to its solid state and hold it at constant pressure so it can be washed

To partially alleviate this problem, as well as to stop the reaction at a reasonable yield and get rid of the excess monomer, the subphase is removed and the film washed [8] after the material has been deposited and condensed at a constant pressure. This cleansing is accomplished by means of an alteration of the film balance set-up, (Figure 7). One liter of 1M HCl is introduced into the trough from one side while the ferric chloride is drained from the other side. (Equilibration of the two flow rates is achieved by manual adjustment of the draining valve). After the first wash has been completed, another liter of the HCl solution is passed through, followed by three successive washes with water, (one liter each). These five washes take about thirty minutes to complete. Despite this thorough washing procedure, the ferric chloride still destroys the teflon coating after a period of time.

Thus, two remaining problems, or disadvantages, with this chemistry are rather obvious; the severe destructive nature of the subphase and the time loss associated with the washing procedure. Some washing will inevitably be necessary in order to prevent the



**FIGURE 7: ALTERATION OF THE LB TROUGH TO ACCOMODATE WASHING**

polymerization from resulting in too high a molecular weight, but five rinses is rather extreme. (A film of high molecular weight becomes too rigid to be deposited via vertical dipping; the slide would simply rupture the film on its first downstroke and continue to pass back and forth through the hole).

As previously mentioned, the quality of these polypyrrole films definitely warrants any investigation which might improve the processing technique and/or the properties of this material. Therefore, a newly proposed chemistry for making well-ordered LB conductive polypyrrole films is presently being investigated and compared to the previously described system. The goal of this research is to develop a new LB method that uses ammonium persulfate, rather than ferric chloride, as the oxidizing agent, and to evaluate the properties of the resultant films in comparison to ones made using the present chemistry. The following sections explain

the details of this new chemistry and examine both its feasibility as a procedure and the quality of its end product. Results reported herein are far from conclusive, but they do provide a good indication of the possibilities for this system and whether or not further investigations should even be made.

### **3.0 EXPERIMENTAL PROCEDURES**

#### **3.1 PROPOSED CHEMISTRY**

Since the root of the only drawbacks of the  $\text{FeCl}_3$  system is the  $\text{FeCl}_3$  itself, the newly proposed method introduces an oxidizing agent which still serves as initiator to both polymerization and doping. Ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , dissolved in 1M HCl, is the experimental subphase in this new polypyrrole LB system. This chemical is much less corrosive than the ferric chloride, so it would not cause as much, if any, damage to the trough and fewer washes should be required.

#### **3.2 BULK FILM PRODUCTION**

Prior to the commencement of any in-depth studies of the compatibility of this system to LB procedures, preliminary experiments were performed so that bulk properties of the polypyrrole (PPY) made using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (PPY-2) could be compared to those of the polypyrrole made using ferric chloride (PPY-1). To obtain a bulk film of PPY-2, a beaker containing 0.5 wt%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in solution with one molar hydrochloric acid was used. By means of a pipette, pyrrole monomer was carefully dropped onto the surface of this subphase, although some of it still sank to the bottom. The reaction was allowed to proceed for ten minutes, at which time the film was horizontally lifted out with a pre-cleaned glass slide that had been rinsed with chloroform.

Two samples of PPY-1 were made similarly, using 5% and 1%  $\text{FeCl}_3$  in purified water. (All water used in our LB work was purified by means of a Millipore reverse osmosis system in conjunction with a Milli-Q<sup>TM</sup> purification system). Finally, another persulfate experiment was set up without using HCl to see if it was really necessary.

### 3.3 CONDUCTIVITY AND STABILITY MEASUREMENTS

All three films were left to dry in the air and were then prepared for conductivity measurements to be taken. First, a small square section of each film was isolated using a razor blade. Next, the slide was taped to a piece of paper, as were four thin gold wires which served as the four point probes. Figure 8 shows this set-up. The gold wires were attached to the films at the four corners using electrodag (an alcohol solution containing fine graphite/carbon fillers); this ensured good contact and prevented the wires from scratching the film.

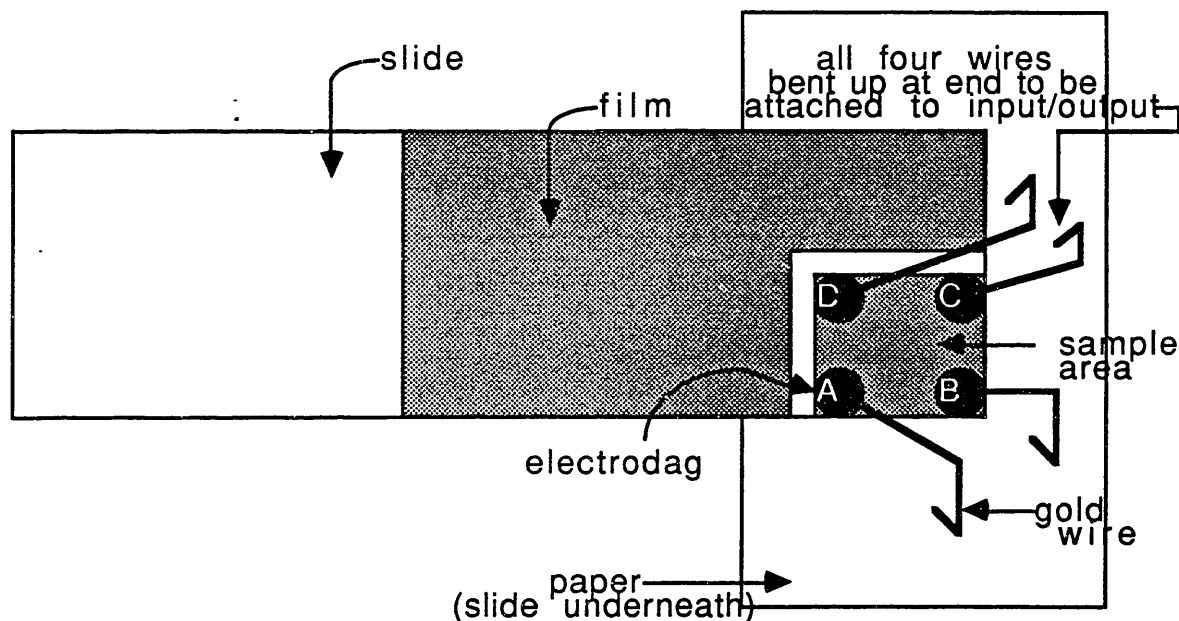
Finally, in-plane (ip) conductivity was measured by applying current across one side of the square ( $I_{AB}$ ) and measuring the voltage across the parallel side ( $V_{CD}$ ). The input and output were then rotated  $90^\circ$  and the voltage  $V_{BC}$  was measured. In both cases, several current values were used to increase accuracy. The resistance was calculated ( $R=V/I$ ) and the average taken for each arrangement. The ratio of these two resistances was used to determine  $f$ , a factor that accounts for any anisotropy (see the Appendix). Lastly, the thickness of the sample ( $d$ ) was measured so the resistivity could be calculated, using the following equation:

$$\rho = \pi d f (R_1 + R_2) / 2 \ln 2 \quad (1)$$

where

$$R_1 = V_{AB}/I_{CD} \quad \text{and} \quad R_2 = V_{AD}/I_{BC} . \quad (2)$$

Of course, conductivity is simply the reciprocal of resistivity. Sample measurements and calculations for each film are found in the Appendix. These measurements were taken repeatedly for a few weeks to determine the stability of the film in its oxidized state. Thickness of the sample was measured using a Sloan Dektak II. An average value was estimated from the resulting plots for use in the calculations.



**FIGURE 8: FOUR-POINT PROBE ARRANGEMENT**

### 3.4 MONOLAYER CHEMISTRY

Many variables were involved in determining the best chemistry for PPY monolayer fabrication, but knowledge of the ferric chloride system at least provided a starting place. Trials were first performed in beakers, then moved to the trough when observations indicated the probable formation of a monolayer at the interface. Parameters that were varied for these experiments include concentration of the oxidizing agent and the components and concentration of the spreading solution. Room temperature was an operating condition, but, for the beaker experiments, it was not regulated in any way.

In all of these reactions, the ammonium persulfate was dissolved into 1M HCl. Subphase solutions were made using as-received chemicals and the previously mentioned ultra pure water. Pyrrole monomer was mixed with varying amounts of 3ODOP, (prepared according to the synthesis described in [9]), and chloroform ( $\text{CHCl}_3$ ), then deposited onto the subphase surface using a

syringe. The approximate amount of monomer required to obtain a single monolayer of the surface-active material was calculated using the known area/molecule of a PPY monolayer, the surface area of the spreading solution, and the known thickness of the monolayer. (The thickness is about 28 angstroms as determined by X-ray diffraction [10]). At first, this value was at least quadrupled so that monomer behavior and polymer formation would be visible. As the ideal conditions were approached, the amount used was decreased to the required value in the hopes of producing a true monolayer.

Once a spreading solution and subphase combination was found that exhibited good dispersion at the interface and produced controllable amounts of polypyrrole, the rest of the experimentation was performed in the trough. Mole ratios of pyrrole to 3ODOP ranged from 500:1 to 5000:1, usually either without chloroform or in a solution of one milligram 3ODOP to one milliliter  $\text{CHCl}_3$ .  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  concentration was varied from 0.01wt% to 0.2% and the reaction time from a couple of minutes to two hours. In most cases, washing was not performed although a few trials included several rinses. After the allowed reaction time had passed, or the washes were completed, the film was then compressed. Isotherms were plotted for verification of the formation of a good monolayer and for later use in determining a suitable pressure for transfer to a substrate. After the surface area had decreased to a very small value, the barrier was stopped and the film was scraped up onto a zinc selenide slide for FTIR analysis (if the trial appeared to have some success).

### **3.5 INFRARED AND OPTICAL ABSORPTION**

Fourier transform infrared transmission spectra were recorded using a Bio-Rad Digilab Division FTS-40 infrared spectrometer. Samples were scanned 256 times at a resolution of  $4.0 \text{ cm}^{-1}$  and a collector sensitivity of 1.5. For further evaluation of the material produced, optical spectra were also recorded from 16 scans on an Oriel Instaspec 250 multichannel analyzer. The light source was a halogen lamp while the light detector was a diode

array of 1024 detectors. The optical data provided quick insight as to whether or not a conductive material had been produced.

## **4.0 RESULTS AND DISCUSSION**

The first experiments to be performed were bulk polymerizations of both systems, as well as one  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  trial without any HCl. These three films were then compared using FTIR, optical, conductivity, and stability studies to determine the quality of PPY-2 samples. Once these investigations were complete, experimentation continued towards the goal of developing a successful chemistry for production of LB films. As parameters were varied, visual observations were made. Both FTIR spectra and isotherms were examined to evaluate the quality of the new polypyrrole and compare it to the other PPY.

### **4.1 BULK FILMS: PPY-2 VS PPY-1**

#### **4.1.1 GENERAL OBSERVATIONS**

To make bulk films, the oxidizing agent is usually in excess of the amount used for LB work, but this was not favorable for the ferric chloride sample. The film made using 5%  $\text{FeCl}_3$  was too thick and took too long to dry for our purposes, so only the 1% sample was evaluated. The other two films were quite satisfactory at an ammonium persulfate concentration of 0.5%; the monomer reacted just as quickly but required less oxidizing agent than did the ferric chloride sample.

At the beginning and end of each reaction, the pH was measured since it is an important parameter in the polymerization of polypyrrole. An acidic environment is paramount to successful polymerization because it considerably inhibits the formation of simple dimers and other oligomers which would otherwise occur. The PPY-2 film made without HCl would reveal the true importance of this parameter and if, indeed, the acid was necessary. If not, the subphase would be even less damaging to the trough. Both the  $\text{FeCl}_3$  and the  $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{HCl}$  solutions maintained a pH of about zero throughout the reaction. The one without HCl, however, started at pH=5.5, but ended at a pH of roughly 2. The implications of this pH

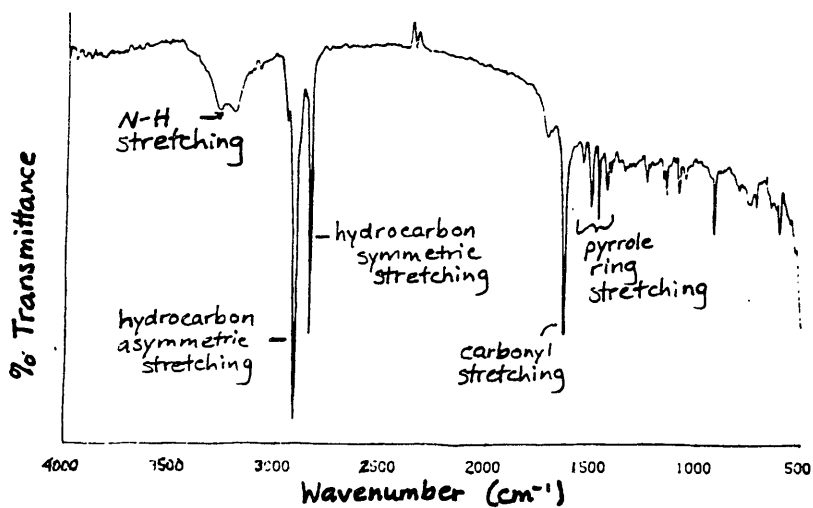


drop are not yet fully understood, but interest in the conductivity of this sample quickly escalated.

#### 4.1.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

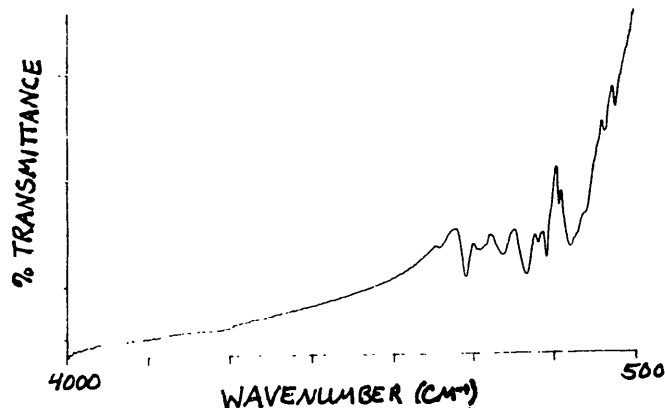
The first analysis to be performed on the PPY-2 sample made in the presence of HCl was FTIR. This method of analysis takes advantage of the absorption phenomenon exhibited by atomic bonds. Bonds between atoms are somewhat flexible and have stretching, bending, torsional, and oscillatory motions associated with them. Many of these bonds possess characteristic frequencies in the infrared range of the electromagnetic spectrum and will, therefore, absorb such energy when it is applied to the material. Different atomic bonds and groups absorb different wavelengths of the incident IR beam, so the constituents of a given sample can be determined.

In the case of pyrrole monomer, the characteristic spectrum includes bands representing the N-H stretching (wavenumber = 3200  $\text{cm}^{-1}$ ) and pyrrole ring stretching (3 absorption peaks around 1500  $\text{cm}^{-1}$ ). Polypyrrole has an additional peak associated with the ring stretching due to its slightly altered state; the change in the bonding at the 2,5 positions enhances the ring motion. In its purest form, these are seen as one big peak centered around 1500  $\text{cm}^{-1}$ . Figure 9 shows a PPY/3ODOP spectrum and the relevant peaks.



**FIGURE 9: FTIR SPECTRUM OF PPY/3ODOP SHOWING KEY PEAKS**

The FTIR spectrum of the PPY-2 (made in 1M HCl) was examined in consideration of these characteristic bands and determined to be identical to that reported for PPY-1 elsewhere [7]. Figure 10 shows the spectrum obtained for our sample.

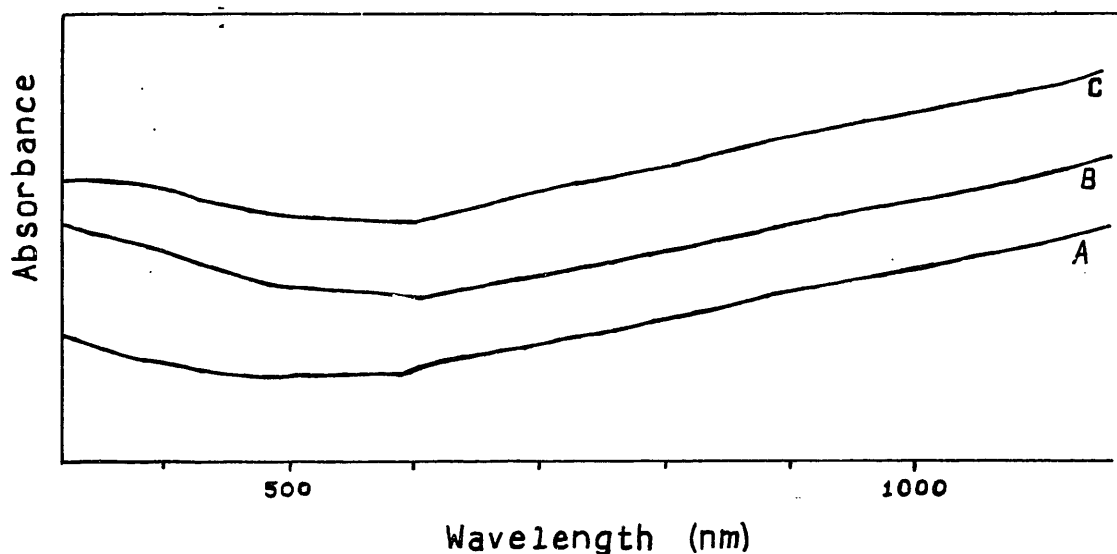


**FIGURE 10: FTIR SPECTRUM OF BULK PPY-2**

#### **4.1.3 OPTICAL PROPERTIES**

Now that PPY-2 had been verified to be pure polypyrrole, the next step was to evaluate its conductive state. This was accomplished by means of optical absorption spectra. Bipolarons are also known to absorb electromagnetic radiation, but, in contrast to the atomic groups previously mentioned, they absorb in the visible region. A broad band centered at a wavelength of about 1300 nm and continuing to near infrared regions is characteristic of these free charge carriers in a homopolymer.

Optical spectra were recorded for all three samples, results are shown in Figure 11. Comparison of the plots reveals great similarity among the films; all three contain bipolaron bands that initiate at the same wavelength. Not only is PPY-2 conductive, but, according to these data, it should have comparable conductivity to PPY-1. Also interesting was the presence of bipolarons in the PPY-2 that was not made in the presence of HCl. Its optical spectrum indicated that it was very similar to the other two samples. Thus far, both means of producing PPY-2 looked promising.



**FIGURE 11: OPTICAL SPECTRA OF BULK PPY; (A) PPY-1, (B) PPY-2/HCL, (C) PPY-2/WATER**

#### **4.1.4 CONDUCTIVITY**

Conductivity measurements of the bulk films also indicated that PPY-2 was comparable to PPY-1. Average values resulting from the previously described calculations were approximately 3.0 S/cm for PPY-1, 1.5 S/cm for PPY-2 with HCl, and 0.4 S/cm for PPY-2 without HCl. The accuracy of these values was only as good as an order of magnitude due to the manner in which the thickness was determined.

No bulk film is going to be very smooth, but the polypyrrole samples tended to crinkle quite a bit, containing many ridges. Therefore, average thickness was by no means an exact value, but rather an educated guess based on a range of thicknesses in a sample line that was only one millimeter long. (See the Appendix for a sample graph obtained from the Dektak). Fortunately, we were not interested in extremely accurate measurements, just in values good enough to make a general comparison of the two films. More accurate thicknesses, and thus more reliable conductivity values, could be measured for LB samples of these materials.

Due to this error inherent in the thickness measurements, conductivities within the same order of magnitude were assumed to be equivalent. Therefore, PPY-2 with HCl was considered to be of the same quality as PPY-1. The sample without HCl had a lower conductivity as originally expected.

#### 4.1.5 STABILITY

The final investigation of the bulk films concerned the stability of the oxidized state over time. Conductivity measurements taken periodically for a few weeks were the means by which stability was observed. Figure 12 shows plots of conductivity vs time for each sample. Excessive fluctuation was demonstrated by the sample made without HCl while the other two remained fairly constant.

The considerably wide range of values exhibited by the PPY-2 sample made without HCl could be the result of many problems that were encountered during the tests. First of all, the contacts were somewhat loose when a couple of the data points were taken. At

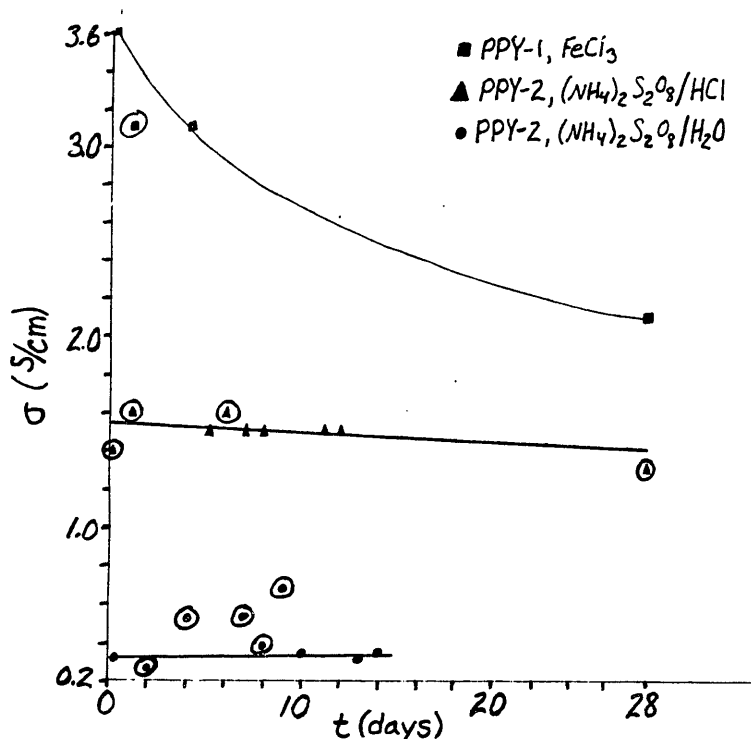


FIGURE 12: CONDUCTIVITY VS TIME

these times, considerable fluctuation was seen in the voltmeter measurements, probably a result of incomplete contact. The gold wires were reattached after the second and the sixth data points had been taken; each was followed by a significant change in conductivity. An apparent alternative may have been simply to make another sample, but this would not have solved the problem. All films that were made without HCl were extremely delicate and flaked off the slide quite easily. Because of this problem, and the lower conductivity, HCl was deemed a more favorable environment for the polymerization of PPY.

The PPY-2 sample made in HCl also experienced some variations in conductivity, but to a much lesser degree. This can probably be accounted for by voltmeter error and changes in humidity, which slightly alter the ability of the PPY to conduct electrons. This PPY-2 sample appeared to be very stable, even in comparison to the PPY-1 film. The latter dropped significantly after almost three weeks, although this fact is based on only one measurement. The main point is, however, that the PPY-2 with HCl was again proven to be comparable to PPY-1.

#### **4.2 PPY-2 MONOLAYER CHEMISTRY**

Now that the new subphase of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in 1M HCl had been verified as suitable for making good bulk conductive polypyrrole films, the next step was to perfect the chemistry on the trough so that highly ordered LB films could be made. Key observations in determining the success of a particular spreading solution and subphase were purely visual; a rippling effect that proceeds across most of the surface with each drop of the spreading solution and a cohesive layer of polypyrrole at the interface (this would be brown in color, with a metallic shine if it's conductive). Indicators of a poor spreading solution were drops that formed little islands or sank into the subphase. Another bad sign was the formation of 'fingers' of polypyrrole that emanated from the surface and shot down into the solution.

In this case, excess pyrrole was polymerizing first, then sinking; not enough 3ODOP was present to keep it at the surface and

the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  concentration was large enough to quickly polymerize all of the monomer in the solution. The goal became two-fold: to have a low enough concentration of persulfate so that these fingers would not form and permeate the entire subphase, yet to keep it high enough to polymerize the pyrrole immediately upon contact, thus preventing the loss of all of the monomer into the subphase. A final significant visual observation was the appearance of fine black lines at the surface upon collapse of the film. White lines, however, indicated monomer. In both cases, the lines were the result of the monolayer folding over on itself and thus becoming thick enough to be seen.

#### **4.2.1 GENERAL OBSERVATIONS**

The first experiment, performed in a beaker, was done with 0.1%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and the 5000:1 solution from the  $\text{FeCl}_3$  system. Observations were made of this trial and parameters were then varied until the reaction behaved according to the ideal conditions mentioned earlier. When a stable surface layer was observed and the spreading solution appeared to serve its purpose, subsequent experiments were done on the trough. Results are only reported for the trough experiments since they are the important, more informative ones. Conditions of each experiment and visual observations are reported in Table 4.

**TABLE 4: PYRROLE POLYMERIZATION EXPERIMENTS ON THE LB FILM BALANCE**

SAMPLE NUMBER	SPREADING SOLUTION <sup>a</sup>	AMMONIUM PERSULFATE	REACTION TIME <sup>b</sup>	WASHES	RESULTS
1	500:1	.05%	0	0	white
2	1000:1:1	.01%	0	0	white
3	1000:1	.05%	0	0	swirls in subphase, dark black lines
4	1000:1:1	.05%	30 min	0	white
5	1000:1:1	.05%	120 min	0	solution filled w/PPY
6*	1000:1:1	.075%	37 min	0	grey lines invisible residue
7	1000:1:1	.1%	30 min	0	some residue
8	1300:1:1	.05%	30 min	0	white
9	1600:1	.05%	0	0	reacted quickly trough not clean
10*	2000:1:1	.05%	30 min	0	good black lines
11	2000:1:1	.05%	5 min	1L HCl 1L water	no lines visible clean trough
12*	2000:1:1	.05%	10 min	1L HCl 1L water	grey lines no mess
13	2000:1:1	.05%	15 min	2L water	white/grey
14	2000:1:2	.05%	35 min	2L water	light grey
15*	2000:1:1	.2%	0	1L HCl 2L water	swirls drained with washing
16*	2000:1:1	.2%	5 min	1L HCl	lots of invisible residue
17	5000:1:1	.05%	0	0	extreme excess

a Concentration is mole ratio of pyrrole monomer:3ODOP:CHCl<sub>3</sub>

b Zero reaction time indicates immediate compression of the film

Many of these preliminary attempts at monolayer formation resulted in excess polypyrrole that dissipated throughout the entire subphase. Again, this occurrence is highly undesirable since these particles could easily become incorporated into the film when it is being deposited onto a substrate, and thus create tremendous disorder. Each of the variables seemed to affect the amount of excess PPY in the same way; an increase in monomer concentration, ammonium persulfate concentration, or in time all resulted in more polymer.

Chloroform, another factor in this chemistry, was determined to be advantageous in the spreading solution. Without it, some of the droplets did not spread as well and became concentrated in their own islands; these places saw the first polymerization. A final condition for the production of high quality thin films was an extremely clean trough. Soon discovered was the fact that the polymerization reaction will more quickly initiate at nucleation points such as spots of PPY left from a previous trial, islands of concentrated PPY, or flaws in the teflon (which were present in our trough as a result of many ferric chloride experiments). Such sites would often result in the premature formation of PPY, starting from the bottom of the trough upward. Consequently, the trough was emptied of any subphase, cleaned thoroughly with chloroform, and soaked in water after each of the later experiments. Soaking in 1M HCl for a half hour and then water is also a good idea at the end of the day.

Results indicate that in order to use a 1000:1 pyrrole:3ODOP solution of lowest persulfate concentration, the reaction time required lies somewhere between 30 and 120 minutes (from Table 4). This time is less than ideal, so the persulfate concentration was increased. Since reaction times were still in the vicinity of 30 minutes, and good black lines were not observed, the pyrrole content of the spreading solution was increased. Following reason like this, parameters were varied until a good film was produced without excess polymer pervading and lingering in the subphase.

Table 4 indicates the best trials, as determined by visual observation, with an asterisk. Of the five 'successful' experiments,



sample 10 was clearly the most ideal. Good, black lines formed and no residue was found in the trough upon cleaning. Also, no washes were needed and a half hour reaction time is moderate enough for such a good film. Although this sample was not washed, it would later be necessary since the reaction would otherwise continue after the half hour was over, and would eventually produce excess PPY during dipping. Thus far, this fact is of the least concern because this experiment has not proved to be reproducible. The failure of a second trial using the same conditions was confirmed by FTIR spectra, as discussed in section 4.2.3.

#### **4.2.2 ISOTHERMS**

The two conflicting factors that needed to be balanced were the need for an instantaneous reaction so that the pyrrole monomer would not dissolve and the desire for a slow enough reaction to prevent incorporation of the PPY into the 3ODOP layer. With a slow enough reaction, the 3ODOP surface layer could be compressed before any pyrrole enters it, resulting in the formation of a PPY monolayer directly beneath the 3ODOP. Again, this was only partially achieved in the ferric chloride system. To be successful, enough of the surface active agent must be present to attract the pyrrole monomer and keep it suspended just below the surface.

The indication that this organization might be possible in the new system was that the isotherms of identical samples compressed at different times resulted in phase changes that corresponded to different areas per molecule. Figure 13 shows the isotherms of a few of the samples, representing a variety of parameter values. Two of the samples shown, 10 and 13, used 60 microliters of a 2000:1:1 (pyrrole:3ODOP:chloroform) spreading solution. Sample 13, which was compressed after only 15 minutes, has an area per molecule of 3ODOP of about 45 sq. angstroms when it first begins to condense. Sample 10, which had a reaction time of 30 minutes before compression, has a much higher value, 60. The implication is, therefore, that since sample 10 spent a longer time in its gaseous state, the pyrrole monomer had plenty of room to incorporate itself into the 3ODOP monolayer and polymerize there.

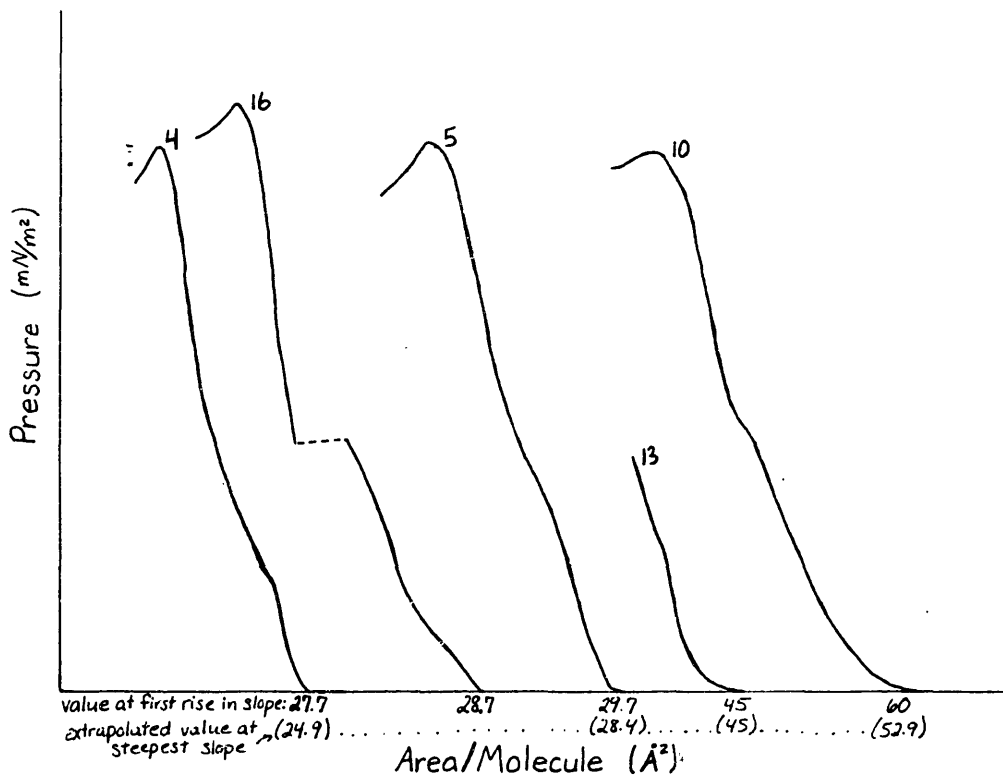


FIGURE 13: ISOTHERMS OF SAMPLES 4, 5, 10, 13 & 16

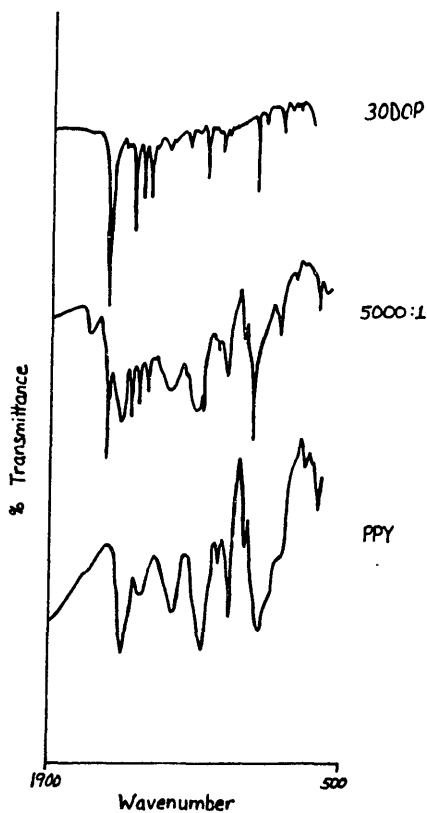


FIGURE 14: REPORTED FTIR SPECTRA OF 30DOP, P/30DOP (5000:1) AND BULK PPY

Samples 4 and 5 were also identical spreading solutions, but the time was varied even more significantly. Sample 4 was allowed to react for 30 minutes, while sample 5 reacted for two hours. The difference in area/molecule at the initial point of compression, however, was only about 2 angstroms/molecule. Since this variation was not very big, the important time frame for incorporation of the pyrrole into the 3ODOP layer seems to be the first half hour. These results also mean that the polymerization is not instantaneous; if it were, the isotherm would always look the same, independent of time. Further investigation is needed before any valid conclusions can be drawn.

A final point of significance concerning the isotherms is demonstrated by sample 15. The dashed line in its isotherm in Figure 13 represents an annealing time, 30 minutes in this case. During this time, the molecules in the film are allowed the chance to reorganize and become more closely packed, filling in the 'holes' in the monolayer. This is evidenced by the decrease in area/molecule that occurs while the pressure is kept constant. In order to produce the most highly ordered LB films, therefore, an annealing time should probably be allowed.

#### **4.2.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY**

Examination of the samples was, therefore, done in light of the other two goals; low processing time and low oxidizer concentration. Trials were initially narrowed down according to the amount of pyrrole residue and the appearance of the black lines, as mentioned in section 4.2.1. This group was then evaluated by means of the FTIR spectra, verifying the amount of polymer actually present in the samples.

The primary peak of interest in this analysis was a fourth absorption peak occurring around  $1500\text{ cm}^{-1}$  due to polypyrrole ring stretching. The size of this was observed in comparison to the primary 3ODOP peaks: i.e., the asymmetric and symmetric stretching of the hydrocarbon chain at  $2900\text{ cm}^{-1}$  and  $2800\text{ cm}^{-1}$ , and C=O stretching at about  $1650\text{ cm}^{-1}$ . Figure 14 shows the spectra of 3ODOP, the ferric chloride PPY, and pure bulk PPY, as reported in

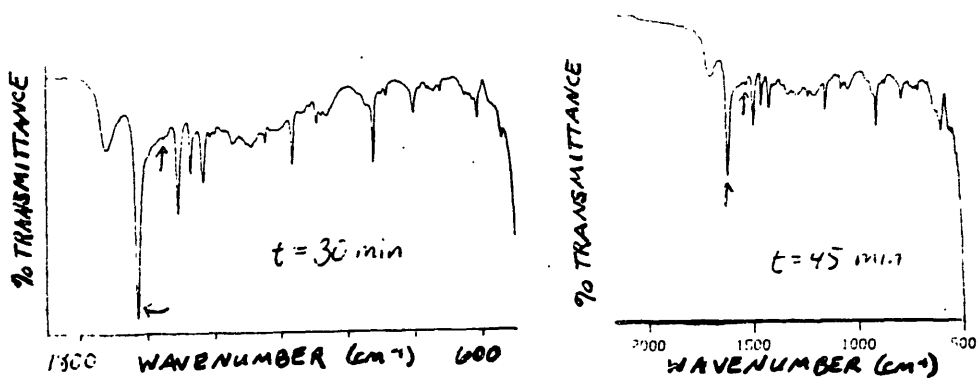
[10]. The 5000:1 solution (B) displays a decrease in 3ODOP bands and an increase in the polypyrrole ones due to the presence of both in the monolayer that was formed.

This analysis was invaluable since, in a few cases, the spectra showed that some of the samples that appeared to be polymer were actually monomer. (Primarily the ones that formed grey lines in the trough). The spectra were also useful in determining trends as parameters were varied. Figure 15 shows the effect of time, spreading solution, and oxidizing agent on pyrrole content. Arrows indicate the two relevant peaks; the larger one is representative of 3ODOP and the smaller one represents PPY. Although a small variation in these parameters would often result in drastic differences in what was seen in the trough, these changes did not always seem to affect the surface film as much.

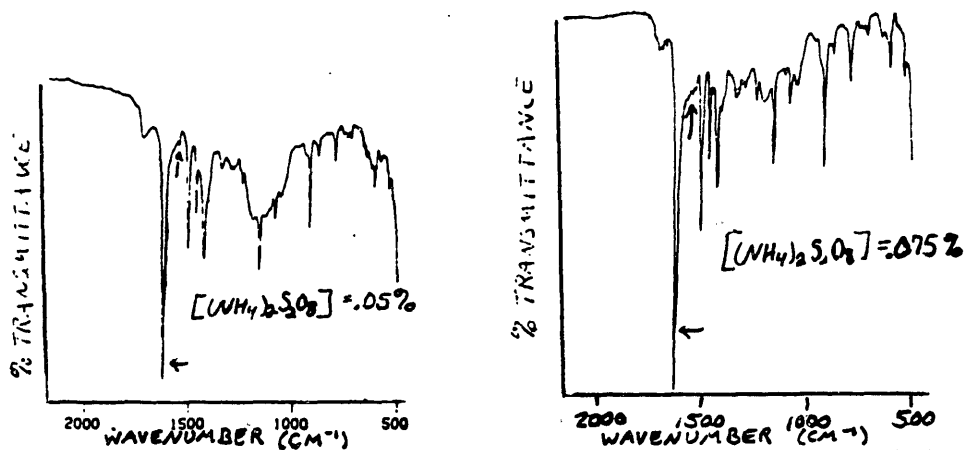
Figure 15a reveals a small increase in pyrrole content due to an extra 15 minutes of reaction time. In the 45 minute sample, the fourth polypyrrole ring stretching band is bigger in comparison to the C=O stretching band of the 3ODOP than it is in the 30 minute sample. The extra 5 minutes given to the 35 minute sample did not seem to result in any significant difference. Comparing these two peaks in the spectra of Figure 15b reveals that a small increase in persulfate content does not really increase the polypyrrole content, although the .075% ammonium persulfate sample formed darker lines in the trough than did the .05% sample. Finally, Figure 15c shows that increasing the pyrrole/3ODOP ratio does, in fact, increase the pyrrole content of the film.

FTIR was also employed to compare two duplicate experiments. Sample 10, one of the most successful as far as spreading and cleanliness go, had the best IR spectrum of all. Upon an attempt to reproduce these results, however, this analysis revealed inconsistency.

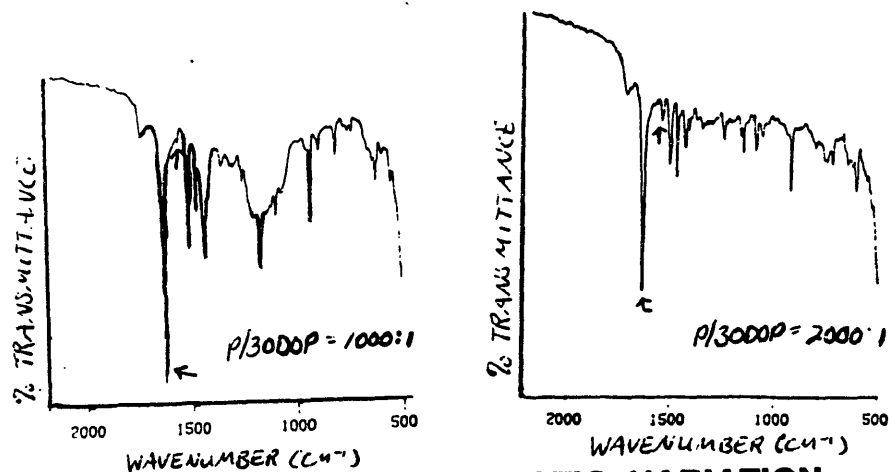
The FTIR spectra found in Figure 16 display the good results obtained for sample 10 and the unimpressive results obtained from the duplicate experiment. Sample 10 did not have a clearly visible fourth ring stretching peak, while sample 15 had had a very pronounced one. Since the spreading solution for sample 10 was



**a: TIME VARIATION**

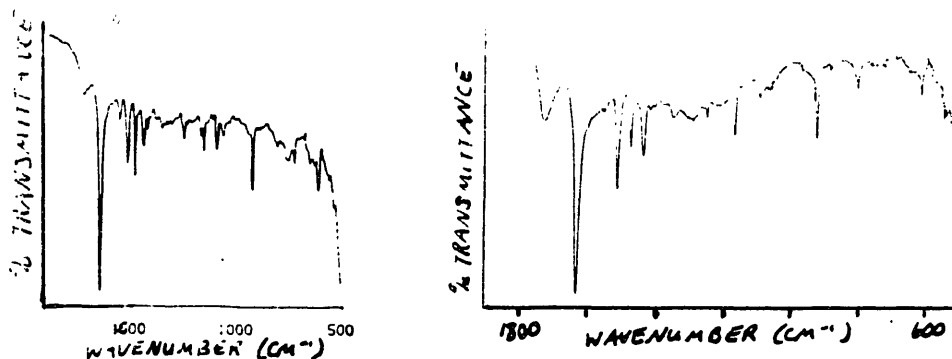


**b: OXIDIZING AGENT CONCENTRATION VARIATION**



**c: PYRROLE/3ODOP RATIO VARIATION**

**FIGURE 15: EFFECT OF PARAMETER VARIATION ON PPY CONTENT OF FILMS MADE ON THE TROUGH**



**FIGURE 16: FTIR SPECTRA OF REAL AND SUPPOSED 2000:1:1 SAMPLE SOLUTIONS**

created by simply diluting a previously used solution, perhaps the concentration was not calculated correctly. Another problem with this solution that was encountered involved the pyrrole used to make the mixture. We discovered that it had dissolved the plastic that had been on the inside of the cap of the bottles in which we were storing it. This would greatly alter the concentration and, therefore, the experiments. (Samples 8 and 9 had also been made from this pyrrole).

Although the best sample proved to be a mystery, subsequent experiments that were performed using it as a basis had some promising results. A 2000:1 mole ratio of pyrrole to 3ODOP still seemed to be the most successful. Sample 15 appeared to have the best results and would probably serve as a good film for the first dipping experiments. Preliminary dips were, in fact, performed on a couple of the earlier samples to evaluate the feasibility of creating multilayer thin films from this chemistry. Results of these quick trial dips reinforced the idea that the films must be flexible; the importance of stopping the reaction after a relatively short time again found significant validity. Also discovered in these investigative deposition attempts was that PPY-2 does not adhere well to hydrophobic glass slides; a coating of about six layers of 3ODOP monomer was necessary for good, uniform deposition.

Results of these investigations have led to the use of a 2000:1:1 spreading solution in LB film production. With this solution and a persulfate concentration of 0.2%, LB multilayer films are presently being produced with much success. A total reaction

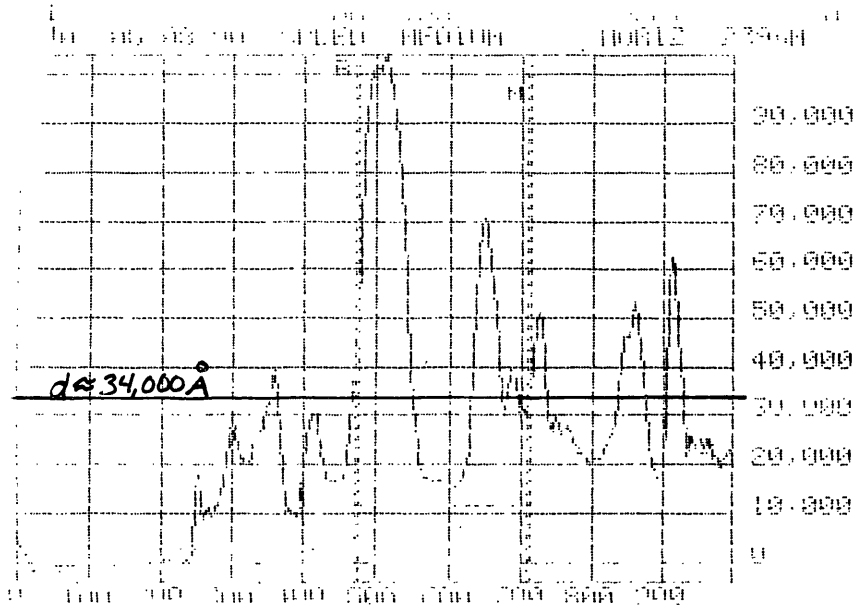
time of 7 minutes from deposition to washing has been used, along with three washes; 1L of .5 M HCl and 2L of water.

## **5.0 CONCLUSIONS AND RECOMMENDATIONS**

Investigations of the new  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  chemistry suggest a superior method for LB production of polypyrrole conductive thin films, as compared to the present  $\text{FeCl}_3$  system. Conductivity of PPY-2 was found to be close in value to that of PPY-1 and quite stable over time, affirming the possibility of using this new chemistry. Preliminary LB experiments demonstrated that a solution of 2000:1:1, along with a subphase containing 1M HCl and 0.2 wt%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , can be used to produce a monolayer of polypyrrole quite efficiently. Complete analysis of the properties of this material has not yet been performed, nor has full characterization been attempted. The degree of structural order must also be determined.

Recommendations for further work in the perfection of this chemistry would include the variation of time and persulfate concentration using the solution from sample 10. Another possibility is to increase the concentration to a value between 2000:1 and 5000:1 since the latter is known to result in an instantaneous reaction and overwhelming amounts of excess PPY while the former might be improved upon if an even lower reaction time can be used. Before attempting this, however, some LB films should be made using the chemistry of sample 15. Characterization and the evaluation of material properties would give great insight as to the true success of the ammonium persulfate procedure. The results of various analyses such as dichroic FTIR, small angle X-ray scattering, and capacitance could be compared to similar studies that have been done on PPY-1. If these analyses also indicate a good material, reproducibility could also be evaluated by studying capacitance and optical properties vs sample thickness. Only then would the true worth of this newer method be known.

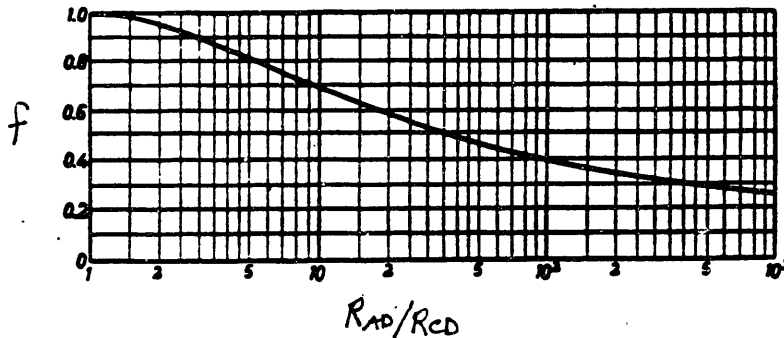
## 6.0 APPENDIX



I	V <sub>AD</sub>	V <sub>CD</sub>	R <sub>AD</sub>	R <sub>CD</sub>
$1 \times 10^{-6}$	-.00064	-.00032	640	320
$-1 \times 10^{-6}$	.00058	.00027	580	270
$-5 \times 10^{-6}$	.00299	.00143	598	286
$5 \times 10^{-6}$	-.00305	-.00149	610	298
$10 \times 10^{-6}$	-.00607	-.00295	607	295
$-10 \times 10^{-6}$	.00602	.00288	602	288

averages:      606      292

$$R_{AD}/R_{CD} = 606/292 = 2.08 \Rightarrow f \approx .95 \text{ from below}$$



$$P = \frac{\pi(34000 \times 10^{-8})(606 + 292)(.95)}{2 \ln 2} = .0657 \Rightarrow \sigma = \frac{1}{P} = 1.52 \frac{\%}{cm}$$



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