Investigation of Degradation in Polythiophene-Fullerene Based Solar Cells

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Investigation of degradation in polythiophene-fullerene based solar cells

by

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# TABLE OF CONTENTS

## ABSTRACT

## 1 GENERAL INTRODUCTION
1.1 Organic Solar Cells
1.2 Poly(3-hexylthiophene) and its properties
1.3 Fullerenes and their properties
1.4 Literature survey of degradation mechanisms in P3HT in solution
1.5 The degradation of P3HT-based devices
1.6 Modeling device degradation - Accelerated Lifetime Testing
1.7 Preventing device degradation

## 2 EXPERIMENTAL ANALYSIS
2.1 Experimental Setup
2.1.1 Standard Cleaning Procedure
2.2 Experimental Parameters
2.3 Measurement Plan
2.3.1 Hole Mobility Measurements using the Space-Charge Limited Current (SCLC) Model
2.3.2 Ultraviolet-Visible Absorption Spectrophotometry
2.3.3 Raman Spectroscopy
2.3.4 Photovoltaic Current-Voltage Characteristics

## 3 RESULTS AND ANALYSIS
3.1 Hole mobility measurements using SCLC model
3.2 UV-Vis Absorption Spectrophotometry
3.3 Raman Spectroscopy
3.4 Photovoltaic Current-Voltage Characteristics

## 4 CONCLUSIONS AND RECOMMENDATIONS
4.1 General Conclusions
4.2 Recommendations for Future Work

## 5 REFERENCES
ABSTRACT

This dissertation investigates the degradation of conjugated polymer poly(3-hexylthiophene) (P3HT). Specifically, exposure of polymer solutions to air and light, and aging of thin films in air and dark has been probed. Solutions of either P3HT or blend of P3HT and phenyl-C61-butyric acid methyl ester (PCBM) were mixed in air and light, and also in dark and inert atmosphere. Thin films of these solutions where then spin coated for UV-vis and Raman characterization. Hole only diodes and photovoltaic devices were also realized and characterized for mobility measurements and photovoltaic performance. Characterizations were repeated after aging the thin films in dark and air for two weeks, and then again after a short annealing at elevated temperature. PCBM was found to reduce the magnitude of P3HT degradation. Solutions mixed in dark and argon were found to respond with a reduction of absorption characteristics when annealed. Solutions mixed in light and air were found to respond with an increase in absorption characteristics when annealed.
1 GENERAL INTRODUCTION

1.1 Organic Solar Cells

In one hour, more solar energy strikes the earth than the combined energy consumed by humanity in one year. If this resource could be harnessed, the total average power that could be generated dwarfs any other fossil-based energy resource available [1]. With the current energy issues in developed countries - including cost of oil and global warming - low cost solar cell and photovoltaic devices have become a very attractive area of research. Currently, the global solar electricity market grosses approximately $10 billion per year, with a 30% per annum growth rate [2]. Unfortunately, due to the tremendous cost and scalability hurdles of solar cell conversion today, namely the power-per-dollar ratio, fossil fuels remain entrenched as the energy source of choice today.

As compared with the traditional inorganic semiconductor technology, organic or polymeric-based solar cells represent a very economical form of solar-to-electric conversion [3]. This is particularly due to the properties of polymeric materials. Commonly, materials of this family are very easy to process and very easy to design chemically (and henceforth, very cheap). In addition, many of the less conventional properties - flexibility, for instance - allow for very novel devices and applications. Finally, because polymers are so chemically different, the variance of polymeric material properties is nearly endless [4, 5]. These advantages mean that polymeric materials are suitable for roll-to-roll processing or low temperature processing, can have variable optical absorption coefficients and are easily tuned by chemical doping - which is not actually a required process in fabrication of these solar cells.
Organic semiconductors in general are comprised of delocalized $\pi$ electron systems. Small, conjugated organic molecules like this are found as absorbers in natural systems as well - for example, $\beta$-carotene or chlorophyll [6]. These conjugated systems allow for both photonic absorption and charge carrier transport. Phthalocyanine and perylene are a good example of organic molecules used for organic solar cells. Pthalo cyanine acts as an electron-donating (p-type) material, while perylene acts as an electron accepting (n-type) material [7].

It is important to note that p and n type nomenclature in organic electronic materials does not indicate doping as it does in crystalline materials. Instead, the nomenclature refers to the relative energy levels of constituents of the device. The material with the lowest unoccupied molecular orbital (LUMO) level closest to vacuum level will spontaneously donate photoexcited electrons to the other material. The former material is called the p-type material, leaving the other material to be called n-type. The materials then transport holes and electrons to the anode and cathode, respectively.

Although doping is not required due to the type of charge transport associated with organic and polymeric semiconductors, it remains a viable area of research with the object of trying to increase the mobility of organic devices. Some groups have shown that extra reagents can be used to increase charge carrier mobility [8, 9], while others show that photochemical doping can induce free charge carriers [10, 11].

Poly-3-hexylthiophene:phenyl-C61-butyric acid methyl ester (P3HT:PCBM) based solar cells are the most studied solar cells to date. The general power conversion efficiency of P3HT:PCBM solar cells is $\sim$5% [12]. The maximum efficiency of conjugated polymeric solar cells is currently 6-8%, as shown by some groups [13, 14].
Thus, polymeric photovoltaics are close to achieving efficiency numbers greater than 10% in the not too distant future. It is at this point that polymeric solar cells will reach dollar-per-watt ratio levels competitive with their inorganic counterparts, at least for off-grid and consumer electronic applications.

Although polymeric solar cells are making progress in efficiency, stability remains an issue yet to be solved. It is known that many polymeric semiconductors are susceptible to degradation in ambient atmosphere. However, most research thus far has been in the synthesis of new polymeric semiconductors or in the device architecture, with the objective of achieving better efficiencies. There are very many stability questions which need to be answered with the same rigor. Variables such as presence or absence of air or humidity (or both), along with the presence or absence of light are important to the stability of polymeric solar cells. Mechanisms of degradation could be further clarified - including molecular degradations of a polymer or interfacial degradations. In addition, interesting questions can be asked - for instance, once degraded, can device characteristics be recovered by any treatment? These and other questions will be the central theme of this dissertation.

1.2 Poly(3-hexylthiophene) and its properties

P3HT is an electronic polymer of the polythiophene family, a family of conjugated-bond polymers known for their conductivity and various uses in the field of organic electronics. In addition to solar cells, P3HT has also been utilized to demonstrate other devices like light-emitting diodes and transistors. P3HT consists of a thiophene ring with a hexane 'tail,' polymerized at the 2- and 5- carbons as shown in Figure 1.1.
When polymerized, P3HT exhibits a conjugated double bond system; that is, alternating single and double bonds. In 1976, this conjugated double bond system was noted by Heeger and MacDiarmind to conduct as well as some metals [16]. Conjugated bond systems are also well known in the fields of organic chemistry and biochemistry as molecules that absorb light. In fact, the degree of conjugation corresponds inversely to the wavelength of light absorbed; that is, longer conjugated molecules can absorb photons of much lower wavelength.
Because of the chiral nature of the P3HT monomer, the polymer can be synthesized in a regioregular or regiorandom form, as is shown in Figure 1.2. For industrial or device applications, it is generally preferred to use the regioregular form, as this form exhibits a carrier mobility of at least two orders of magnitude higher than that of regiorandom forms [17]. This is due to the existence of more crystalline regions - more regular polymers can form more ordered lamellar structures.

1.3 Fullerences and their properties

Buckminsterfullerene (or buckyball) is a well-known structural form of carbon that greatly resembles a soccer ball. Many small differences exist in the structure of various version of buckminsterfullerene, which has led to the christening of a class of
molecules simply called 'fullerenes.' Of this class of materials, PCBM is often used in organic solar cells in conjunction with P3HT.

Figure 1.3: Poly-3-Hexylthiophene:phenyl-C61-butyric acid methyl ester (PCBM) [18]

Fullerenes were determined by Sariciftci et al. [19] to have the ability to accept transferred electrons from conducting polymers, making it an excellent n-type organic molecule. Its ability to dissolve properly in many organic solvents make PCBM a particularly excellent choice for polymeric photovoltaics and other conducting-polymer applications.

Further research has been done by researchers to determine properties of PCBM. One important study by Al-Ibrahim et al. [20] shows that PCBM has an estimated LUMO level of -3.75 eV, which is more negative than the estimated LUMO level of P3HT, -3.53 eV. This makes it an excellent electron acceptor - very little energy is lost in the transition from P3HT to PCBM. In the same study, they also show that PCBM has a lower HOMO level than P3HT (-6.1 eV compared to -5.2 eV), which keeps it from donating electrons to (or accepting holes from) P3HT. [20]
1.4 Literature survey of degradation mechanisms in P3HT in solution

As has been determined by many groups, P3HT degrades in the presence of light and air via a process that reduces charge carrier mobility. Degradation also takes place in the presence of heat, but at a much slower pace [21]. This degradation can reduce the lifetime of photovoltaic devices and is an undesirable property for any optoelectronic application in general.

It has been shown that the method of degradation involves an oxygen attack on the first carbon of the alkyl side chain of P3HT [21]. The reaction is pushed toward degradation using the energy of photons or thermal energy. Subsequent energy causes a free-standing free radical hydroxide and a free radical oxygen paired to the first carbon of the alkyl chain. These free radicals go on via various reactions to add alcohols, ketones, and carboxylic acids to the alkyl chain. In some cases, these reactions cause the scission of the alkyl chain altogether, resulting in extra hexyl- biproducts (including aldehydes and carboxylic acids) In addition, the hydroxide free radical can attack the sulfur on the thiophene ring, resulting in oxidation of the sulfur [21]. These reactions do not directly disrupt the conjugation of the P3HT backbone.
Figure 1.4 Alkyl degradation pathways as suggested by Manceu, et al. [21]

UV-vis analysis studies done by Chang, et al. has indicated that the degradation of P3HT does in fact cause a disruption in its conjugated backbone [22]. It has been noted that the existence of sulfinate esters correspond to the disruption in the conjugated bond structure. Since the only viable source of sulfur (the main qualifier between sulfinate esters and other esters) in the system is the thiophene ring, it is assumed that the oxidized sulfur in the above reaction eventually becomes the sulfinate ester in question [21].

X-ray diffraction studies, also done by Chang et al. suggested that the alkyl reactions drastically disrupt the regularity of the P3HT crystal structure, inducing flaws and defects. Because of the nature of charge transport, these polycrystalline and amorphous areas reduce the mobility of P3HT [22]. This makes all degradations
reactions undesirable for photovoltaic applications - not simply the reactions attacking the conjugated structure.

Earlier research on these degradation reactions suggested that a singlet oxygen played a pivotal role in the breaking of the polymer backbone. However, this theory has been rejected by Abdou and Holdcroft [23]. By bubbling singlet oxygen through a test solution of P3HT for 16 hours, they determined that very few free radical hydroxides were created. However, the FTIR signature of sulfines and carbonyl groups were observed, suggesting that singlet oxygens do participate in the alkyl reactions [23].

1.5 The degradation of P3HT-based devices

Several groups have studied the degradation of P3HT based thin films and devices. Though specialized in terms of parameter space, these studies do help shed light on additional degradation parameters and possible incompatibilities (unexpected reactions/instabilities leading to lowering of mobility) of P3HT with various materials. Many papers (including the ones detailed above) suggest more hopeful findings than could have been expected; that is, that P3HT is a moderately robust material in terms of compatibility.

Auger electron microscopy can be done on a sample while using argon sputtering to strip the sample away layer by layer. This technique can be used to determine the relative fractions of various elements in each layer, and is useful for determining degradation information. Such an experiment was used by Zimmerman, et al. [24] to shed some light on degradation in P3HT:PCBM solar cells. It was found that during processing in the presence of air, the contacts of the devices can oxidize - especially near the contact/semiconducting layer border. This oxidation can reduce conductivity.
Interestingly, the contacts are more likely to oxidize than the semiconducting layer, and certain contacts are more likely to oxidize than others. The total efficiency of the device decreases as a function of this oxidation - hence, as a function of this oxidation.

For some time, the oxidation of the contacts was under question - in particular, it was unknown how much an effect the contacts of the device had compared to the active layer itself. [25, 26] The question was whether the active layer itself caused lower performance in the device, or whether the interface between the contacts and organic layer was more important. Reese et al. reported that the metal/organic interface of an organic photovoltaic cell was a significant contributor to the device's overall degradation, and more important compared to the active layer. [25]. This was determined by depositing contacts on one half of a sample, allowing the samples to 'soak' in constant illumination, depositing contacts on the other half of the sample, and measuring the differences between the two [25]. As stated, greater degradation was observed due to metal/organic interface than the active layer.

Additional studies of degradation due to contacts show that some contacts - particularly calcium/aluminum contacts - can exhibit void formation, contributing significantly to the degradation of device performance [26]. In addition, some contacts show an increase in work function over time due to their oxidations - silver is an excellent example of this. This increase in work function is disadvantageous for electron-collecting contacts. This oxidation can occur in the dark as well as in light, as reported by Lloyd et al. [26]. It was determined that the organic layer did not significantly decompose while stored in the dark - even in air [26].
This investigation under this dissertation uses these variables, in addition to others. In particular, the effect of annealing (in heat and simply in an argon soak) and the effect of PCBM on degradation features are studied. Rather than discovering the precise mechanism or mechanisms of degradation, the goal of this study is to elucidate which parameters are affected by degradation, including structural, photophysical, electronic, or optoelectronic. Structural aspects were characterized by Raman spectroscopy, photophysical by UV-Vis absorption, electronic aspects by mobility measurements using the space-charge limited current model, and the overall optoelectronic properties were characterized by photovoltaic measurements. Finally, differences in gold and aluminum contacts, while not directly studied, can be determined from the data taken.

1.6 Modeling device degradation - Accelerated Lifetime Testing

Little data seems to exist on degradation models alone. Many groups use degradation models in conjunction with operation models. The most explicit version of degradation modeling comes in the form of accelerated lifetime measurements (ALT), and only gives data on a normalized time of degradation. One such study that developed ALT for organic photovoltaics comes from Schuller et al. in 2004 [27].

Schuller et al. studied the polymer poly[2-methoxy-5-(3′-7′-dimethyloctyloxy)-1,4phenylene vinylene] (MDMO-PPV) in a blend with PCBM. In particular, Schuller et al. attempted to determine the degradation constant of this polymer and fit it to one of three different lifetime test models. It was found that the Arrhenius-Modell model best fits the acceleration of degradation due to the chosen accelerated lifetime testing. The model is shown below as equation 1.1 [27].
This model relates the degradation constant \((k_{\text{deg}})\) to activation energy of a process, Boltzmann's constant, and temperature \((E_a, k_B, \text{and } T\) respectively). The degradation constant is a constant that scales a certain quantity according to the time that a sample is exposed to a certain atmosphere. In particular, Schuller et al. exposed their MDMO-PPV/PCBM devices to 40°C under a light setup of approximately 1/3rd natural sunlight. The chosen scaling quantity was short circuit current \((I_{SC})\), such that

\[
I_{SC}(t) = I_{SC}(0)(1 - k_{\text{deg}}t)
\]

This model works moderately well for devices, though it does not relate properties of a material to its degradation constant. Instead, the degradation constant is almost entirely due to temperature. However, this degradation constant is an extremely useful tool for accelerated lifetime tests and determining 'normalized time' of a test.

The accelerated lifetime test model was used by De Bettignies et al. on a P3HT:PCBM solar cell to determine the differences of various processing techniques [25]. They reported that a mixture of 1:1 by mass of P3HT:PCBM has a short circuit current of greater magnitude than other mixtures (specifically 1:2 and 1:4), in addition to a greater fill factor. They also reported that annealing a P3HT:PCBM solar cell at 100°C causes a gain in UV-Vis absorption, possibly increasing quantum efficiency [28].
1.7 Preventing device degradation

In order to create robust devices capable of sustained operation in ambient working conditions (that is, air and room temperature), many researchers have been pursuing air stable setups or materials. The most popular method of degradation prevention is encapsulation - placing a completed device inside a transparent, airtight barrier.

The simplest version of encapsulation is to encase the device between two glass plates. As long as the glass plates are thin enough to allow a maximum of light to reach the device, this solution works very well for blocking ambient air from reaching the device. However, this method greatly reduces the robustness of the overall cell by increased fragility. In addition, it does not allow for the flexibility so desired in organic applications [29]. Instead, this method is best suited for an academic research lab setup to protect the device from degradation while performing characterizations.

Researchers have been working with various other encapsulating techniques. One such technique, suggested by Dennler et al., is to encase a device (made of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene--vinylene) (MDMO-PPV) mixed with PCBM in a poly(ethylene napthaline) (PEN) derivative barrier [30]. In order to reduce the already minimal air flow into the device, this encapsulation apparatus was also filled with an unreactive gas. Because PEN is a naturally flexible polymer and because the encapsulation is filled with gas, the cell is easily bent without too much strain on the active layer and its contacts. The device in question showed an increase in shelf life from a few hours to a full 3000 hours when encapsulated in PEN rather than PET - another common encapsulation mechanism [30].
In order to properly characterize photovoltaics with encapsulation methods - and to transport them to other labs - a standard of encapsulation must be created. This reduces possible chemical incompatibilities and allows for more standardized testing outside of an inert glove box - particularly when time-sensitivity is a device issue. Krebs suggests a very simple method of encapsulation that can easily be standardized [31]. This method requires that the device be fabricated on a glass substrate, and then encapsulated between glass and aluminum using a glass-fiber-reinforced thermosetting epoxy. This is also a very simple method to set up and use - once ready, the method requires only a twelve-hour cure time, in addition to the few steps required to make the encapsulation itself. Krebs reports that a device left in encapsulation for a year suffered only a 65% decrease in efficiency [31].

A novel approach to protecting devices from degradation is the insertion of a protection and scavenging layer. This was attempted by Lee et al. [32] A titania layer, when placed in between different layers of a device with a polyfluorene (PF) active layer, showed various protection effects. The most striking effect was seen when the titanium oxide layer was placed on both sides of the PF layer or on the 'air' side of the PF layer. However, a scavenging effect was noted as well: when the titania was placed 'behind' the PF layer - that is, with the PF closer to air than the titania - it was found that degradation was still reduced compared to the non-titania device. Over a fifteen hour period, devices treated with titania layers showed negligible degradation [32].

The real test of a polymeric solar cell encapsulation setup comes in the form of an outdoor lifetime test. Hauch et al. showed P3HT:PCBM devices that remained stable for one year in the climate specific to Lowell, MA (USA). In addition to this outdoor
lifetime test, Hauch et al. showed an encapsulation setup that survived a 1000-hour accelerated light test. This encapsulation setup used PET as the substrate and an unnamed transparent barrier film to protect from ambient air as shown in Figure 1.5 [33].

![Figure 1.5 Cross section of outdoor device setup [33]](image)

This outdoor device exhibited some strange characteristics. Between October 2006 and March 2007, the power output increased to a maximum of 140% its original value, then hovered between 140% and 120% in a fashion that was directly related to the average outdoor temperature. From May 2007 to the close of the test, the device began a linear decline to 80% of its original power output value. Hauch et al. report that the open-circuit voltage of the module decreased by a total of 6.8% over the test, while the overall efficiency of the device increased by 3.31% [33].

Recently, Vitex Systems [34] has developed an encapsulation material called Barix™. Barix™ is a proprietary system using alternating layers of a polymeric and a barrier material. The barrier material is nearly impermeable to air and water, while the polymeric system serves to help decouple and eliminate intrinsic defects in the total system. Because of the nature of the system, Barix™ requires a deposition of liquid
precursor stage and a nucleation of barrier layer stage. This method of encapsulation creates a very flat surface, with geometry on the order of 10 angstroms [34].
2 EXPERIMENTAL ANALYSIS

This section will discuss the experiments done under the umbrella of this dissertation to study the degradation of P3HT and P3HT:PCBM thin films and devices. The steps below outline the setup of devices and solutions along with the designed experimental parameters. Finally, the measurements selected will be detailed.

2.1 Experimental Setup

Solutions were started by mixing a 1:1 ratio (by mass) of P3HT (acquired from Sigma-Aldrich) and PCBM (acquired from Nano-C). These mixtures were then dissolved in dichlorobenzene (DCB) at a concentration of 10 mg/mL. Solutions were then subjected to the parameters discussed in Experimental Parameters while being mixed with a magnetic stir bar.

Figure 2.1: Device Sandwich Layout
Measurements were done on sandwich-style devices shown in Figure 2.1. 1 inch square glass substrates were procured with Indium Tin Oxide already sputtered on one side. All slides were cleaned using a standard clean procedure detailed below. A poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) in water procured from Clevios P was applied to the ITO side of each glass slide by spin coating at 3000 RPM for 100s on a Headway Research Photoresist Spinner. Each slide was covered and allowed to anneal at 120ºC for 5 minutes in air.

After annealing the PEDOT:PSS layer, slides were transferred into an MBraun 20G argon glove box and spin coated on a Specialty Coating Systems G3P Spincoater with their respective solutions at 600 RPM for 30 seconds. All slides were then covered, wrapped in foil, and allowed to solvent anneal overnight (16-24 hours). Slides were then masked and deposited with their selected metal (either gold, using a Temescal BJD-1800 Electron-Beam Evaporator, or aluminum, using an already existing home-built thermal evaporation chamber). One corner of the remaining polymer surface area was then swabbed with chloroform to expose the ITO layer. Devices were then released for testing.

2.1.1 Standard Cleaning Procedure

Up to three ITO slides were stacked in a centrifuge tube full of a 1:1 mixture of acetone and isopropyl alcohol by volume. The centrifuge tube was then submerged in an 8891 Cole-Parmer Ultrasonicator and sonicated for 7 minutes. Upon completion of the sonication step, slides were removed from the acetone/IPA tube and manually agitated in deionized water. The slides were then stacked into a centrifuge tube containing deionized water treated with Alconox Detergent. This entire process (sonication, agitation) was repeated in the detergent, and the slides transferred to a solution of 1:1 ethanol and
methanol by volume. The sonication and agitation process was completed again. Then the slides were transferred to a final centrifuge tube of deionized water. This tube underwent the sonication and agitation process one final time.

Slides were then removed from the DI water centrifuge tube and dried by passing dry nitrogen over all surfaces. Next, slides were placed inside a Harrick PDC-32G oxygen plasma cleaner. The slides were exposed to oxygen plasma for one minute. Finally, the slides were visually inspected before being allowed to proceed to other steps.

2.2 Experimental Parameters

For the setup detailed above, both solutions and devices were subject to various experimental parameters. During their mixing cycles, solutions were either kept in light from an Electrix 120V, 60Hz, 22W fluorescent lamp and ambient air, or were shrouded in dark by aluminum foil and kept in the argon glove box. In addition, solutions were either made with P3HT or P3HT:PCBM. Devices, after initial measurement, were stored for two weeks in ambient air and the dark. A second set of measurements was done for samples at this point, and then devices were subjected to a 30 minute, 140ºC heat anneal before one final set of measurements was taken.

Table 2.1 shows a summary of experimental parameters.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting 1</th>
<th>Setting 2</th>
<th>Setting 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light exposure</td>
<td>Fluorescent lamp</td>
<td>Dark</td>
<td>N/A</td>
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<tr>
<td>Air exposure</td>
<td>Ambient air</td>
<td>Argon</td>
<td>N/A</td>
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<tr>
<td>Solution composition</td>
<td>P3HT</td>
<td>P3HT:PCBM (1:1)</td>
<td>N/A</td>
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<tr>
<td>Contacts</td>
<td>Gold</td>
<td>Aluminum</td>
<td>N/A</td>
</tr>
<tr>
<td>Measurement Point</td>
<td>After spin coating</td>
<td>After 2 week soak</td>
<td>After 30 minute anneal</td>
</tr>
</tbody>
</table>

**Table 2.1** Experimental Parameters

### 2.3 Measurement Plan

As previously mentioned, devices underwent measurements at three particular times - immediately after spin coating, after 2 weeks of soaking in ambient air, and after a 30 minute anneal (which followed the 2 week soak). The following characterizations were performed on the thin films and solar cells:

1. Hole mobility measurements using the SCLC model
2. UV-Vis Absorption Spectrophotometry
3. Raman Spectroscopy
4. Photovoltaic Current-Voltage Characteristics

#### 2.3.1 Hole Mobility Measurements using the Space-Charge Limited Current (SCLC) Model

This measurement was done by connecting each device to a Hewlett-Packard 4156A Semiconductor Parameter Analyzer and applying a voltage between the ITO base and the gold contacts. Current as a function of this voltage was then measured.

Raw data was analyzed via the Space-Charge Limited Current model proposed by Mott and Gurney [35], as given in equation 2.1. Voltage and the natural logarithm of current were plotted against one another and fitted to a logarithmic function (such that an
equation of the functional form of $\ln(J) = A\ln(V) + B$ was found, where $A$ and $B$ are constants. The data was then analyzed using the rearranged Mott-Gurney SCLC equation and mobility as a function of layer thickness was extracted.

$$J = \frac{9\varepsilon \mu V^2}{8L^3} \quad Eqn\ 2.1$$

$$\ln(J) = \ln \left( \frac{9\varepsilon \mu}{8L^3} \right) + 2\ln(V) \quad Eqn\ 2.2$$

Where

- $J$ = Current Density
- $\varepsilon$ = Dielectric Constant
- $\mu$ = Charge Carrier Mobility
- $L$ = Conduction Length (Polymer Thickness)
- $V$ = Applied Voltage

For the purpose of experiment, the thickness of the polymeric material was assumed to be 200nm because the solution concentrations and spin coating parameters used usually lead to such a thickness, as determined from both experience and literature. Although this assumption may not be valid, because the thickness is a static scaling factor, the assumption becomes trivial for the sake of comparison. This measurement was done immediately after deposition of gold-contact devices, two weeks after deposition, and immediately after heat annealing. It was done for both the P3HT and P3HT:PCBM films, and for both light/air exposed and unexposed conditions.

It is important to note that this method gives hole-only mobility. This is because of the work function of the electrode used (gold). Effectively, there are no electron-capturing electrodes, allowing only hole conduction.
2.3.2 Ultraviolet-Visible Absorption Spectrophotometry

This measurement was done on the gold-contact samples, due to area constraints. Samples were placed in a zeroed, calibrated Cary 5000 UV-Vis-NIR Spectrophotometer by means of a home-assembled sample stage. Samples were placed with the polymeric side toward the beam, and measured in transmittance mode. The wavelength range used for the scan was between 900nm and 250nm. The scan rate was set at 600nm.

The transmittance of the sample was converted to absorbance by the simple definition of absorbance, \[ \text{ABS} = -\log_{10}(T) \], where both absorbance (ABS) and transmittance (T) are given in fractions. All samples were analyzed on a plot of intensity vs. wavelength to determine whether any absorption capability was lost due to degradation. This measurement was done immediately after deposition, after the two-week soak, and after heat annealing of all samples was complete.

2.3.3 Raman Spectroscopy

Raman Spectroscopy was done to determine whether samples exhibited Raman active chemical degradation. Samples were placed in a Renishaw inVia Spectrometer set to use the 488nm line of an Ar+ laser at 50 mW power and calibrated to internal silicon reference bands. Spectroscopy was done with radiation from 100cm\(^{-1}\) to 3200cm\(^{-1}\) at standard confocality. Before measurement, an optical microscopic image was taken to be certain that the sample area was of acceptable roughness. At least two measurements were taken in different places in order to determine roughness effects.

This measurement was done only after initial deposition, and therefore only determines the effect of solution degradation and not solid device degradation.
2.3.4 Photovoltaic Current-Voltage Characteristics

This measurement was done on Aluminum deposited samples. Samples were illuminated through the glass side using a GE ELH Bulb, adjusted so that an intensity of 100 mW/cm$^2$ was incident on a single crystal silicon reference cell. Voltage was applied to the samples between the ITO contact and the aluminum contact and current was subsequently measured using a Keithley 276 source measurement unit. Fill factor, shunt resistance, and series resistance were all determined using software programmed in-house on the TestPoint platform.

This measurement was done immediately after deposition, after the two-week soak, and after heat annealing of all samples was complete.
3 RESULTS AND ANALYSIS

This section details the results of the experiment outlined above. Experimental data for each measurement is shown, along with their individual analyses.

3.1 Hole mobility measurements using SCLC model

As noted above, SCLC data was taken at three points in the experiment; immediately after deposition, after a 2 week soak in ambient atmosphere, and immediately after a 30 minute heat anneal at 140ºC (which followed the 2 week soak). This SCLC data is shown below (on a logarithmic chart, for better understanding).

![I-V characteristics of hole-only devices immediately after deposition](image)

Figure 3.1: SCLC data, immediately after deposition
Figure 3.1 simply shows the relative differences between mobilities (directly proportional to the intercept of the data) of each sample. The data suggests that exposure to air and light during solution mixing over a period of 24 hours does not have any effect on the hole mobility of fabricated diodes. There is only a slight difference in I-V curves, which can be due to some small discrepancy or an uncontrolled processing error - for instance, thickness variations in the different samples. Data does indicate that hole mobility of P3HT increases when it is blended with PCBM, as shown by an increase of two orders of magnitude zero-field current in P3HT:PCBM samples than in P3HT samples. This indicates that PCBM reduces interchain overlapping between P3HT chains, which reduces traps at positions when chains intersect, and thus increases mobility. Such an effect has also been reported earlier [36, 37].
Figure 3.2: SCLC data, after a 2 week soak in air

Figure 3.2 shows some degradation in both of the P3HT:PCBM samples, and very little (if any at all) degradation in the P3HT sample in air. Unfortunately, due to an as-yet undetermined error, data for P3HT mixed in dark and Argon is missing from the records. However, this absence does not affect the overall conclusions discussed later in the dissertation.
Figure 3.3: SCLC data, after a 2 week soak in air followed by a 30 minute, 140°C anneal

Figure 3.3, when compared with figure 3.2, shows that annealing caused some sort of immediate degradation in any sample mixed in light and air. It is unknown whether or not this annealing caused a degradation in the P3HT mixed in dark and Argon, due to the missing data in figure 3.2

After analysis with equation 2.2, assuming a thickness approaching 200nm, figure 3.4 (below) was created.
It can be seen that across the board, mobility decreased from the readings immediately after deposition to after a soak/anneal. However, beyond this, each sample seems to have benefited or degraded due to a different step. For instance, the P3HT:PCBM samples whose solutions were mixed in Argon and dark settings experienced a small benefit from the heat annealing, while both the samples mixed in air and light experienced a mobility loss upon annealing (regardless of their solution composition).

In addition, the P3HT sample whose solution was mixed in air and light exhibits a moderate mobility increase with a 2 week soak, which is certainly unexpected. Excepting this situation, however, the soak in air seems to have caused a definite mobility loss. This is also generally true of annealing, though it is unknown whether or not...
annealing is entirely at fault - it may be true that the adsorbed oxygen caused a slow reaction that degraded mobility, and that this reaction was further increased by the presence of heat.

3.2 UV-Vis Absorption Spectrophotometry

UV-Vis spectrophotometry was done at three points in the experiment; immediately after deposition, after a 2 week soak in ambient atmosphere, and after a 30 minute heat anneal at 140ºC (which followed the 2 week soak). It is known from literature data [21] that P3HT absorbs with a characteristic peak with a maximum of 500 nm, a small shoulder at about 550, and another small shoulder just beneath 600 nm. PCBM gives small absorption below 400 nm. Absorption data is shown below.

Figure 3.5: UV-Vis Data, Immediately After Deposition
Figure 3.5 shows the general UV-vis curves immediately after deposition of contacts. In the case of bare P3HT, clearly solutions created in the dark absorb more and are more suited for solar cell applications. In the case of P3HT:PCBM, the absorption difference is not so obvious. It seems as though P3HT:PCBM in the dark has higher absorption characteristics than the same solution in the light, but the difference is slight and within the margin of error. It is interesting to note that PCBM seems to have a notable effect on the degradation of the overall solution. Less of an absorption drop is noted than that of P3HT-only thin films.

![UV-Vis, 2 Weeks After Deposition](image)

**Figure 3.6: UV-Vis, After 2 Week Soak**

Figure 3.6 shows UV-Vis absorption after a 2 week soak in ambient air and dark. A later comparison will be made between all three measurements, but initial study of Figure 3.6 indicates very little degradation of photophysical properties of any thin film, with the possible exception of the sample coated with P3HT:PCBM mixed in air and light.
It is interesting to note that thus far, no red or blue shift has been observed. In addition, degradation of the UV-Vis peaks seems to occur only in the realm of absorption.

![UV-Vis, After 2 Week Soak and 30 Minute Anneal](image.png)

**Figure 3.7** UV-Vis After 30 Minute Anneal at 140°C

Figure 3.7 indicates a very interesting situation. After anneal, both of the samples mixed in air and light seem to have absorption values comparable to their counterparts in argon and dark. At first glance, it is not clear how the solutions mixed in argon and dark fared. To this effect, Figure 3.8 and 3.9 have been compiled and investigated.
Figure 3.8: Comparison of P3HT thin films at various points of the experiment

Figure 3.9: Comparison of P3HT:PCBM thin films at various points of experiment
Figures 3.8 and 3.9 show comparisons of UV-Vis characteristics for each type of thin film. Scales have been adjusted to more fully separate differences in the data.

In the P3HT-only thin films, it is more clear that the exposure to air and light causes reduced absorption compared to mixing in an argon atmosphere in the dark. In fact, at the peak absorption wavelength (around 550 nm), thin films coated from the dark-mixed solutions absorbed 10% more light than the light-mixed solutions.

After two weeks, very small changes seem to have occurred in terms of absorption. Whether mixed in air and light or in argon and dark, absorption remained constant between the initial reading and after two weeks of soaking in air.

However, it is very striking to note the effects of heat annealing. After annealing, P3HT thin films with solutions mixed in light and air exhibited an increase of absorption, though not to the level of the solutions mixed in dark and argon. Conversely, P3HT devices with solutions mixed in dark and argon showed a decrease of absorption - though not to the level of their air/light-mixed counterparts. In addition, these differences make for about a 5% difference in the amount of light absorbed.

In the P3HT:PCBM thin films, conclusions are more difficult to draw. All films seem to absorb about the same amount with very small differences due to treatments. However, some strange trends are observed. First, a two week soak in ambient air seems to have marginally increased the absorption for samples coated with the dark/argon mixture, but decreased the absorption for films coated with the light/argon mixture. As with the P3HT films, however, heat annealing decreased the absorption of P3HT:PCBM mixed in dark and argon, and increased the absorption of P3HT:PCBM mixed in air and light. Hypotheses on these trends can be found in the 'conclusions' section.
3.3 Raman Spectroscopy

Raman spectroscopy was only done immediately after deposition of contacts. It was done in order to determine any Raman specific chemical changes in the solution due to differences in mixture.

![Raman Spectroscopy Immediately After Deposition](image)

**Figure 3.10**: Raman Spectroscopy Comparison

Figure 3.10 shows the Raman spectrograph of each thin film immediately after deposition. On this spectrograph, it is interesting to note that the most characteristic peak (the two peaks slightly beneath 1500 cm\(^{-1}\)) has not shifted at all. However, smaller shifts seem to have taken place - the P3HT:PCBM samples exhibit very small but discernable peaks at a wavenumber only slightly above 1500 cm\(^{-1}\). However, other than these peaks, spectroscopic results appear rather similar for each - suggesting that no Raman specific
chemical change occurs during mixing in light and air compared to mixing in dark and argon.

Additional Raman spectrographs were also taken at different areas around the device. These spectrographs were identical to the previous spectrographs. The lack of any Raman shift across various spots that the thickness in each area was comparable to each other area.

3.4 Photovoltaic Current-Voltage Characteristics

As noted above, photovoltaic current-voltage data was taken at three points in the experiment; immediately after deposition, after a 2 week soak in ambient atmosphere, and immediately after a 30 minute heat anneal at 140°C (which followed the 2 week soak).

Since each device included six to nine contacts, photovoltaic measurements were done on all pads. In order to make acceptable and proper comparisons, the pads with the highest fill factors were chosen (plotting all data makes for a very complex graph).

In addition, as mentioned above, only the devices made of P3HT:PCBM exhibited reasonable photovoltaic behavior, because P3HT-only devices lack an electron acceptor in the donor matrix.
Figure 3.11: PV characterization

Figure 3.12: PV characterization
Figures 3.11 and 3.12 show the progress of degradation due to soak and anneal of devices. In each situation, the fill factor of the device decreases with every subsequent step. Considering the data seen in previous sections, the fact that annealing causes a lowering of the fill factor is worth some note. Furthermore, each subsequent step results in a lowering of short-circuit current, and an increase in open-circuit voltage.

In order to figure out the effect of each solution mixing conditions on PV characteristics, Figures 3.11 and 3.12 have been combined into Figure 3.13.

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**Figure 3.13:** Comparison of PV characteristics between devices

Comparing the characteristics of these two materials shows very few differences - both types have very much the same characteristics. All devices perform nearly equally at each step. However, it does seem clear that the devices whose films were mixed in dark and argon outperform those whose films were mixed in light and air. This is true of
both the two-week soak curve and the annealing curve, especially - though the difference is only 0.05mA.
4 CONCLUSIONS AND RECOMMENDATIONS

This section will present possible conclusions that can be drawn from the results of the experimental work, and will follow up with recommendations for future study and work.

4.1 General Conclusions

By examining the data shown above, some general conclusions can be drawn which may help develop the model of P3HT degradation and assist in building better polymeric-based optoelectronic devices in the future.

The first general conclusion to note is that definite differences exist in solutions mixed in dark and argon versus solutions mixed while exposed to light and air. Solutions mixed in light and air have an initially less desirable characteristics (including mobility and absorption characteristics). However, solutions mixed in light and air are more likely to benefit from heat annealing processes. It is thought that solutions mixed in light and air undergo chain scission (a process whose products are Raman inactive). This chain scission results in weaker absorption and mobility characteristics. In addition, it is possible that with these smaller, more mobile chains, the solution is apt to crystallize more favorably - and possibly even repair chains - when subjected to a heat-annealing process. This re-crystallization process can increase absorption.

The next general conclusion to note is the degree to which PCBM protects from polymeric degradation. Solutions of P3HT that include PCBM tend to absorb similarly throughout soaking and annealing processes. However, it is possible that this is simply
because there are fewer P3HT chains to absorb, so differences in absorption are very low. In addition, though P3HT:PCBM devices performed more desirably in mobility experiments when their solutions were initially mixed in dark and argon, P3HT-only devices performed more desirably when solutions were mixed in light and air. It is suggested, then, that PCBM is protective only in certain situations - and even then, not protective enough to be an adequate defense against degradation alone.

Another general conclusion to be drawn is the effect of heat annealing versus simple air soak. It seems clear that a very small amount of heat annealing after device degradation can have a very large effect. PV characteristics suggest that heat annealing after degradation causes an undesirable loss in fill factor and short circuit current. It is important to note that PV devices had aluminum contacts, rather than gold contacts. As mentioned in other papers [24,25], contacts play an important role in device degradation. We believe that most probably a degradation mechanism is happening between the semiconducting layer and aluminum contact, while an enhancement mechanism (possibly re-crystallization/annealing) is happening inside the semiconducting layer.

4.2 Recommendations for Future Work

The subject of P3HT degradation has some interesting implications which may eventually be applied to other polymeric semiconductors. It would be interesting to see the effects of more variables on the characteristics studied - for instance, controlling humidity during the air soak, or soaking in light in addition to air (a situation well known for degrading P3HT) may be acceptable variables to test. Other variables might include a
sort of 'fatigue' testing - that is, a continuous voltage through the semiconductor to determine the effects of current on degradation.

In addition, the use of different contacts can provide a method for separating degradation and enhancement mechanisms, as also shown by Reese, et al. [25]. It might be interesting to further study the degradation mechanism between aluminum and the semiconducting layer, possibly by substituting various other contacts instead of simply gold.
5 REFERENCES


