Investigating IR switching of dioxythiophene-based conjugated polymers

An Undergraduate Thesis

Callie L. Goins

Signature: John Reynolds

Faculty Mentor: Dr. John Reynolds

School of Chemistry & Biochemistry

School of Materials Science & Engineering

Georgia Institute of Technology

Signature: Will [illegible]

2nd Faculty Reader: Dr. Will Gutekunst

School of Chemistry & Biochemistry

School of Materials Science & Engineering

Georgia Institute of Technology

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Chapter 1: Introduction

1.1: Prior Work & Literature

An electrochromic material is a material that can switch between two different colored states upon application of an electrical voltage which changes the oxidation state of the film. This switching behavior has been studied extensively in the visible region, where existing commercial applications include smart windows and anti-glare rear view mirrors, both of which can tint on-demand to regulate heating/cooling needs in the case of the former and enhance driver safety in the case of the latter (Figure 1). However, the appeal of these materials extends past the visible region, as their spectral modulation continues into the near and midinfrared. Being able to control the infrared absorbance allows for controlling the change in emissivity, or the measure of IR energy radiated, of a material. This application is of major interest to the military as a means to achieve thermal camouflage, as it would make possible a thermal signature undetectable to IR cameras when using these materials.[1] Another potential application of utilizing electrochromic, infrared switching materials is traffic visualization; while technology currently can be implemented into cars and trucks to identify thermal signatures such as that of animals or people, utilizing electrochromic materials could make it possible to identify thermal signatures of traffic lights or signs as well.[2] This application could have a role in reducing crashes and road incidents in low visibility conditions, which would have an impact on drivers everywhere.

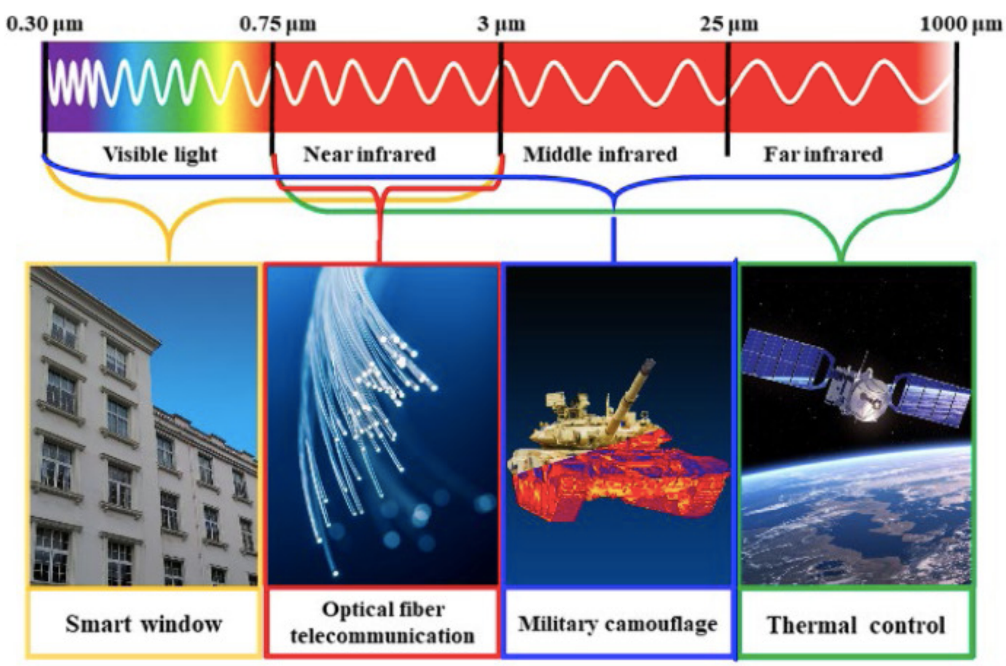

Figure 1. Example of some applications for electrochromism in different areas of the visible and IR spectra of light.[1]

Metals and metal oxides are the most widely studied electrochromic materials for these applications and have previously been studied to much fundamental success.[3] Tungsten oxide (WO_3) electrochromic devices have demonstrated promising IR contrast in the 3-5 micron region, one of the main areas of interest for IR-switching devices.[3] Aside from being examined for IR applications, WO_3 has been used in smart windows, self-dimming mirrors, and other electrochromic visible-region devices.[5] Not only have metal oxides been studied for electrochromism, but metals such as platinum and silver on the nanoscale level have been investigated as well; these two types of materials have differing electrochromic mechanisms, with metals requiring electrodeposition and dissolution and metal oxides switching upon charge introduction with counter ions. Metal oxides have also demonstrated excellent modulation and thermal camouflage abilities, making them candidates for electrochromic devices as well. They have shown stability up to 350 cycles of switching and are able to be used on flexible substrates.[6]

While metals and metal oxide have demonstrated excellent electrochromic properties in the midinfrared, some drawbacks in these materials include the expensive and difficult deposition methods required, such as sputtering techniques, and the tradeoff between stability and fast switching.[1] Meanwhile, conducting polymers, a recently developed class of electrochromic materials, are flexible, lightweight, soluble -- allowing a variety of different deposition techniques to be used when casting thin films.[1] Polymers are not placed onto substrates via the deposition methods used for metal oxides and metals; instead, they are dissolved in a solvent and coated onto substrates via blade coating, spin coating, or spray coating. This is an advantage to utilizing electrochromic polymers over metals and metal oxides; the deposition techniques required of metals and metal oxides are complex and expensive, whereas solution coating can be integrated into high-throughput coating techniques. Previous work has shown that spin coated films exhibit the highest contrast, followed by blade coated and spray coated. However, each is a viable option of the deposition of polymer films onto substrates.[12] These materials also have easily tunable structures for improving IR contrast, making them appealing for continuing to develop a broad range of materials available for electrochromic devices and applications via synthetic methods; through this fine tuning, stable and fast switching materials can be developed, and absorption behavior can be controlled throughout various wavelengths of interest in the IR region.[9]

While studies on IR modulation using polymeric, organic materials have been done in the past, these materials are much less commonly examined. However, there have been excellent results from using conducting polymers for visible light active electrochromic devices, and their performance in this field makes them promising candidates for use in IR modulation. To implement conjugated polymers in electrochromic devices, these conducting polymers need to be able to withstand oxidation and reduction both chemically and electrically. This oxidation and reduction process alters the polymers' visible and infrared spectra, causing the previously discussed switch. Investigation of the properties of conjugated, thiophene-based polymers, such as P3HT, shows how doping, the oxidation or reduction of a polymer, can affect the polaron and bipolaron spectral signatures based on dopant concentration. Polarons appear spectrally as growing absorption peaks throughout an oxidation process, while bipolarons, less readily formed due to counterion position, lead to a blueshifted absorption spectrum when compared to that with a single polaron.[14] Polarons and bipolarons are correlated with hole carriers in the polymer matrix, and chemically and electrically induced holes can be identified and compared.[10] As a polymer becomes oxidized, the neutral state is gradually converted to an oxidized state, giving rise to a polaron. Upon further oxidation, the polaron is depleted and oxidized, forming a bipolaron. The electrochemical doping of polymers such as P3HT leads to the contrast in the IR spectra which is characteristic of IR switching materials, and this doping has an additional effect on the electronic energy levels, resulting in varied IR spectra.[11] Conjugated polymers, such as poly(3,4-ethylenedioxythiophene), or PEDOT, have tunable energy levels and band gaps related to HOMO-LUMO energies and frontier orbital hybridization; these in turn affect the redox properties, which are crucial for electrochromism and conductivity.[8] These polymers are also commonly tuned to reduce band gap, with substitution and conformational adjustment being specifically discussed.[9] The ability to fine tune key properties of these polymers makes these potential structural candidates for IR switching. As further development is performed on IR switching materials, it is important to consider multiple families of polymers and multiple structural features.

Polyaniline has previously been used for IR switching purposes, demonstrating excellent change in emissivity with an application of a voltage, proving the capability of this material in being used for thermal camouflage or satellites, but the modulation was much less than that demonstrated by metal materials previously.[7] However, better results in terms of emissivity change have been found for PEDOT.[2] PEDOT demonstrated excellent stability, fast switching, and thermal contrast of approximately 15%. While slightly lower performing, the IR contrast of PEDOT is comparable to that of metal oxides, and this work demonstrated that these polymeric materials are excellent candidates for future applications, especially upon further optimization.

Typically, an electrochromic device is fabricated with a thin (hundreds of nanometers) layers of the electrochromic material deposited on a transparent conducting electrode, a charge storage material deposited on a transparent conducting electrode, and finally an electrolyte layer sandwiched in between. In the case of an electrochromic device conducting in the IR region, the transparent conductor needs to be invisible in the IR region.[4] The devices previously developed using conjugated polymers, rather than metals, utilized IR transparent substrates and gel electrolyte, along with the polymer being used as both the electrochromic material and the ion storage layer.[2] After seeing the performance of these devices, it is clear that electrochromic polymers are extremely promising candidates for IR applications that can be seen as a supplement to metal-based devices due to high contrast coupled with fast switching and high durability.

1.2: Introduction to this Work

In this study, electrochromic dioxythiophene-based polymers, chosen based on prior successful switching and performance in the visible range, are studied with a focus on their infrared switching properties, with the goal of understanding how structure impacts the contrast between the oxidized state and the reduced state. The high contrasts observed in the visible region found for these polymers, especially when compared with that of metal oxides, is promising for future use of these electrochromic polymers in devices for the mentioned applications. The polymers of this study are divided into three categories: donor-acceptor polymers (with two polymers in this family being initially studied and compared), electron-rich all-donor polymers with alkyl side chains, and electron-rich all-donor polymers with oligoether side chains. To study the differences between the structural groups of these polymers, spectra are collected of polymer thin films on gallium arsenide (GaAs), which is an IR-transmissive substrate. These thin films were chemically oxidized and reduced, allowing for an understanding of the IR spectra for these polymers in both states. Then, prototype devices are constructed. A typical electrochromic device is constructed of a transparent conducting substrate, layer(s) of electrochromic material, layer(s) of electrolyte, and layer(s) for ion storage (Figure 3). The layer of electrolyte comes after the polymer films are deposited onto substrate (and doped chemically if it is required prior to electrochemical doping) to allow it to be electrically switched. Additionally, a working electrode and counter electrode are required for successful switching.[4] For electrochromic polymer devices, the ion storage layer and electrochromic material are the same. These devices are switched by application of electrical voltage, and IR spectra are collected at regular voltage intervals in order to identify contrast and optimum voltage range for said contrast.

Studying both prototype devices and thin film spectra allows for a complete picture of the IR switching capabilities of the selected polymers upon both applied electrical voltages and chemical doping; by identifying the contrast and success of these materials, they can be identified as excellent candidates for IR switching applications. The core of this research lies in both this identification of materials for IR switching applications and the understanding that can be gained about how the structural features of electrochromic polymers affect their IR contrasts. This will lead to improved knowledge of how to best develop electrochromic polymers for infrared applications, aiding the scientific community in creating improved materials for military camouflage, thermal camera imaging, and more.

Chapter 2: Materials & Methods

2.1: Selected Polymers

Four polymers were selected for study in this work, chosen based on previous electrochromic performance in the visible range in terms of quick and reversible switching from a transmissive to an absorptive state. These materials can be divided into three classes: donor-acceptor, alkyl side chain, and oligoether side chain. Two dioxythiophene-based, donor-acceptor polymers were studied and compared here: ProDOT-EDOT-isoindigo-EDOT (P-E-iI-E) and P(ProDOT$_2$-BTD-ProDOT$_2$) - where ProDOT is 3,4-propylenedioxythiophene, EDOT is 3-4-ethylenedioxythiophene, and BTD is benzothiadiazole. BTD and isoindigo are electron accepting units, whereas ProDOT is an electron rich, electron donating subunit. The side chains in these polymers predominantly serve as solubilizing groups. The alkyl side chain polymer was ProDOT-EDOT (PE), and the oligoether side chain polymer was P(OE)$_3$ (where OE is an oligoether subunit). The structures of each of these polymers are shown in Figure 2. All polymers were synthesized and provided by Austin L. Jones of the Reynolds Group at Georgia Tech with the exception of P(ProDOT$_2$-BTD-ProDOT$_2$), synthesized by Anna M. Österholm.

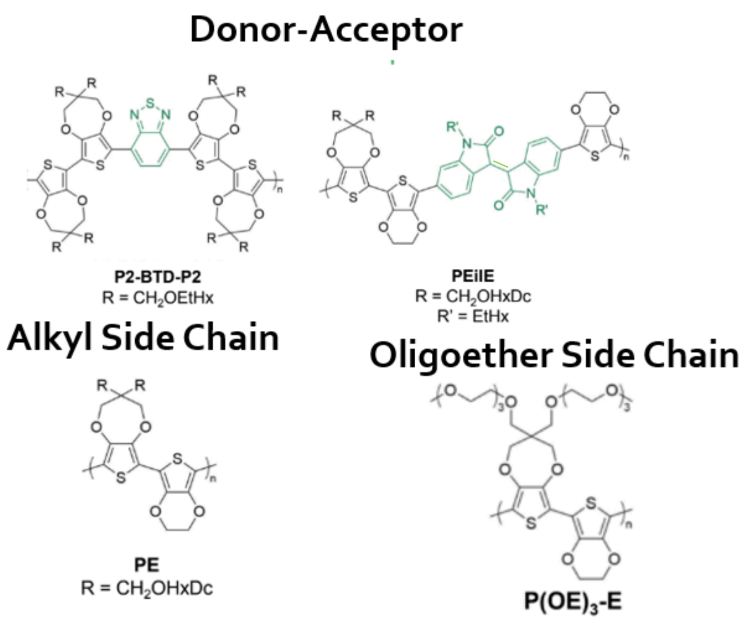

Figure 2. Structures of polymers used. Acceptors are highlighted green in the donor-acceptor polymers.

2.2: Coating of Thin Films on Gallium Arsenide

Thin gallium arsenide substrates, generously provided by Jarrett Vella of the Air Force Research Laboratory (AFRL), were utilized as highly mid-IR-transmissive substrates in this study. These substrates were carefully rinsed with acetone and sonicated 5 min in chloroform in order to clean the substrates; throughout all steps, these substrates were handled gently due to the extremely brittle nature of gallium arsenide. The selected polymers for study were spray coated onto these substrates using an air brush, supplied with nitrogen gas via connection to a cylinder at 10-20 psi, consisting of a spray nozzle (Iwata Gravity Feed Airbrush) and a liquid reservoir, which was filled with a 4 mg/mL solution of the selected polymer dissolved in chloroform. This spray coating was performed by fixing a gallium arsenide substrate firmly in place using double-sided tape and spraying uniformly until the desired thickness was reached. This thickness varied from 227 nm to 1055 nm based on the film and was measured using a Bruker DektakXT profilometer.

In the experiments performed here, some films for each polymer were selected to be oxidized, while others were reduced. For those being oxidized, iron (III) perchlorate hydrate was chosen as the dopant due to its ability to fully oxidize all polymers being studied. 10 mM dopant solution was prepared in 2 mL batches by dissolving the appropriate amount of iron (III) perchlorate hydrate in acetonitrile. For the films being oxidized, this dopant was dropcast onto the film and sat for 5 minutes in order to ensure oxidation prior to soaking the solution up with a Q-tip or KimWipe. For those films being reduced, hydrazine monohydrate was chosen as the dopant. In order to avoid delamination of polymer films, which is likely to occur when hydrazine monohydrate is placed directly onto the thin films, the films were placed into a closed Petri dish adjacent to a KimWipe soaked in the hydrazine monohydrate. The films were allowed to sit for 5 minutes and then removed. All doping was done within a fume hood.

2.3: Device Fabrication

Glass microscope slides were used as the primary substrate for device fabrication; prior to use, they were rinsed in acetone and cut in half (end dimensions: 2.54 cm by 3.81 cm). Next, gold Kapton tape (http://astraltechnology.com/thermal_control.html) was carefully placed, avoiding any bubbles underneath, over one face of the substrate; wells were carefully cut away with a razorblade according to Figure 3 in order to create two separate electrodes: an anode and a cathode. Similar to thin film fabrication, spray coating was utilized as the method to coat the substrates on the same side with the gold Kapton tape with 4 mg/mL in chloroform solution of the selected polymers. The same spray coating apparatus and setup were used. The devices were spray coated with solution uniformly to various thicknesses as needed for the study; for each polymer, repeat devices were made of both similar and varying thicknesses. Thickness was measured using a Bruker DektakXT profilometer. Prior to continuing, a Q-tip and acetone were used to wipe the wells of the device of any polymer film in order to prevent shorting the electrodes.

Next, a blade coater (Zehnter Testing Instruments ZAA2300) was used to coat each device with a thin layer of electrolyte (1:4:7 poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP): 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIBTI):Acetone). The blade height was set to 1500 μm above the surface (400 μm above the substrate) and a speed of 20 mm/s. 200 μL of electrolyte was used for each device, and after blade coating, additional electrolyte was dropcast in 40 μL increments in the wells and on the outer electrode of each device, ensuring optimal coverage for proper switching. Finally, the electrolyte was wiped away using a Q-tip and acetone from the bottom edge of each device, allowing for copper tape to make clean contact with the gold layer as a conducting material to clamp onto for controlling with the potentiostat. For some later devices, this process was optimized, and excess gold Kapton tape was used as the extra conducting material rather than copper tape.

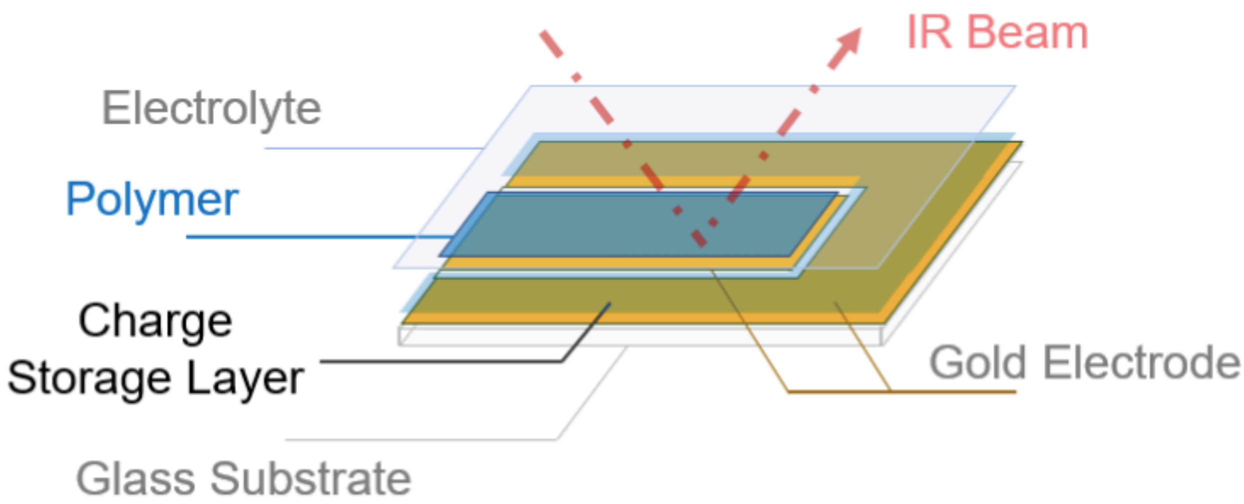

Figure 3. Set up of a typical electrochromic device. For the devices in these experiments, the polymer and charge storage layer are the same.

2.4: Spectroscopic Characterization

A Shimadzu IRAffinity Fourier Transform Infrared Spectrometer (FTIR) was used for the collection of all IR spectra. For thin films on gallium arsenide, transmittance spectra were collected against a blank of a clean piece of gallium arsenide. The measurements were averaged over 32 scans; average transmittance values used were found by averaging across the 3-5 micron range.

For characterization of devices, the devices were connected to a portable potentiostat (Autolab PGSTAT101), with the inner electrode connected to the working electrode wire and the outer electrode connected to both the reference and counter electrode wires. Voltages from -1.0 to 1.0 V were applied in 100 mV increments, and a reflectance spectrum was collected at each point. Reflectance spectra were collected against a blank of clean gold Kapton tape on a glass microscope slide. After proceeding through the entire -1.0 V to 1.0 V range, -1.0 V was applied again to each device. This was done to verify the stability and reproducibility of the devices and measurements.

Chapter 3: Results

3.1: Comparing Contrast in Thin vs. Thick Electrochromic Devices

In developing electrochromic devices for donor-acceptor polymers, it was important to examine how thickness of the device impacts contrast. First, changes in the IR contrast and switching spectra based on film thickness were analyzed; three devices were constructed for each of the two donor-acceptor polymers in this study (P(ProDOT$_2$-BTD-ProDOT$_2$) and P-E-iI-E), and the devices were categorized as thin (approx. 0.5 absorbance), medium (approx. 1 absorbance), and thick (approx. 2 absorbance). For both donor-acceptor polymers, thin electrochromic devices had minimal infrared switching and relatively low contrast in comparison to that of medium or thick devices.

To calculate IR contrast at a particular wavelength, the lowest reflectance (%) value was subtracted from the highest reflectance value at that wavelength, regardless of the specific voltage that the value was from. In Figure 4, the medium and thick devices for P(ProDOT$_2$-BTD-ProDOT$_2$) are shown to be similar in terms of contrast, with the medium thickness device having a contrast of approximately 47% at the 2500 cm^{-1} wavenumber – examined due to its position in the 3-5 micron range of interest to IR detectors – and the thicker device having a contrast of approximately 43% at the same wavenumber. This value represents the difference between the oxidized and reduced state of the electrochromic device.

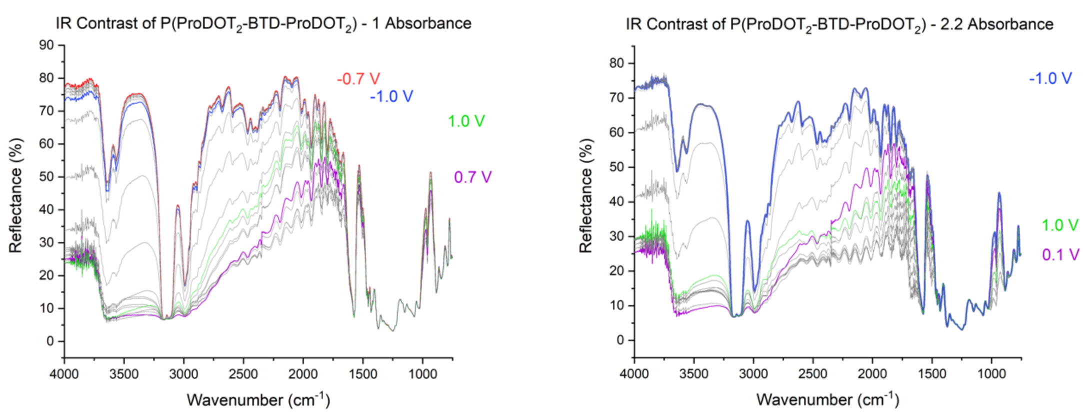

Figure 4. IR switching for donor-acceptor polymer P(ProDOT$_2$-BTD-ProDOT$_2$) at two different thicknesses. These graphs resulted from electrochromic devices with voltages applied from -1 to 1 V and spectra collected in 100 mV increments.

The medium thickness devices for both donor-acceptor polymers had slightly greater contrast than those at a higher thickness and absorbance, but contrast only decreases slightly over a range of thicknesses, giving more freedom of thickness in coating future films. Going forward in experiments, 2-3 devices for each polymer were made to have absorbances of approximately 1 in the visible region to account for the results of this study, but thicker films were prepared to similar degrees of success. Notably, a film of 0.5 absorbance or less will not have a large IR contrast that is notably applicable to the studies of interest.

3.2: Comparing Transmittance vs. Thickness on Gallium Arsenide

Next we examined the relationship between transmittance vs. thickness in the IR region of the two donor-acceptor polymers above – studied extensively in order to both understand inherent properties and potential switching capabilities in devices of these systems. Average transmittances were calculated for each film thickness by averaging all transmittance values in the 3-5 micron range for that particular film. The 3-5 micron range and 10-12 micron range are both of interest to IR switching applications; however, as seen in the above data in Figure 4 and future presented data, contrast is traditionally higher in the 3-5 micron range. Additionally, the electrolyte used in electrochromic devices absorbs more strongly in the 10-12 micron region, so focusing on the 3-5 micron range is more relevant for comparing thin film data with devices.

Transmittance was examined in the oxidized and reduced/neutral states for polymer films on gallium arsenide; however, the reduced/neutral states normally presented transmittances close to 100% that varied much less across films and polymers. In Figure 5, the average transmittance is shown as a function of thickness for the oxidized state of the two donor-acceptor polymers in this study. Both have a relatively exponential decay; any deviation of linearity can be attributed to the difficulty in spray coating films uniformly or to changes in the environment or blank across films and measurements. This exponential comparison of transmittance vs. thickness obeys the Beer-Lambert law.

Interestingly, P(ProDOT$_2$-BTD-ProDOT$_2$) decayed at a much steeper slope than P-E-iI-E as thickness was increased. There was also difficulty in spraying P(ProDOT$_2$-BTD-ProDOT$_2$) films to a thickness greater than 500 nm, suggesting a point in which it is ineffective to study or develop films or devices at higher thicknesses. P-E-iI-E did not have the same issue, easily being sprayed to thicknesses greater than 1000 nm. Multiple different spraying solvents, including dichloromethane and toluene, were tested for P(ProDOT$_2$-BTD-ProDOT$_2$); these yielding the same results suggests that the thinner nature of the films should not be attributed to the solvent but rather to the polymer.

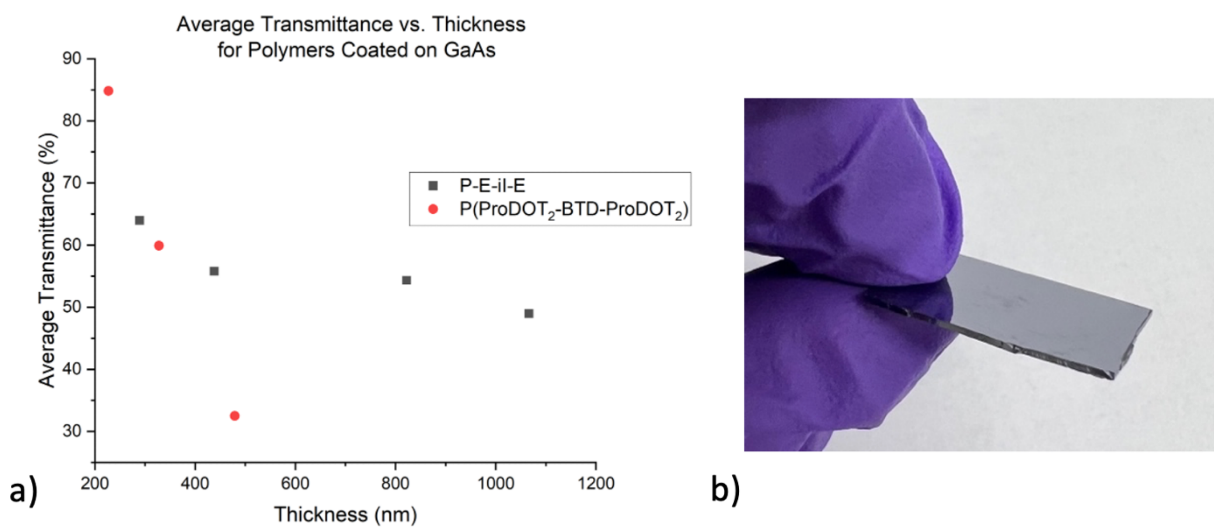

Figure 5. a) Average transmittance vs. thickness of polymer films coated on GaAs for each of the two studied donor acceptor polymers, P-E-iI-E and P(ProDOT$_2$-BTD-ProDOT$_2$). Average transmittances are based on the transmittances across the 3-5 micron region in the film's oxidized state. (b) Gallium arsenide substrate was used for these experiments in thin wafer form.

As shown in Figure 5, investigating transmittance vs. thickness yields a proven correlation; as thickness increases, transmittance decreases, regardless of the polymer or the thickness of the film. This leads to increased contrast when in device form. Medium thicknesses were used for this study, as these demonstrated better contrast than thinner devices without the added difficulty of spraying to higher thicknesses.

3.3: Comparing Various Thicknesses and the Reduced State of Polymers of Different Structural Groups on Gallium Arsenide

After examining the donor-acceptor polymers on gallium arsenide, the three structurally different families of polymers (donor acceptor, alkyl side chain, and oligoether side chain) were also studied using this substrate. For all 3 structurally different polymers in this study, various thicknesses of film were spray-coated onto gallium arsenide and oxidized in order to compare transmittance vs. thicknesses. These results, along with data from other polymers of each family, demonstrated the decrease in oxidized state transmittance for each polymer with an increase in thickness. This decrease was most significant for oligoether side chain polymers, followed by alkyl side chain polymers and donor-acceptor polymers.

An additional study for these polymers was done on gallium arsenide to identify and compare the reduced state across various thicknesses. This was done to ensure that the reduced state transmittance of an electrochromic polymer film does not vary significantly with thickness. Displayed in Figure 6 is the reduced state for each of the three structurally different polymers for a thinner, ~100 nm film and a thicker, ~300 nm film. For each of these, there were no significant differences (especially P-E-iI-E). While there was variance between the two films for the oligoether side chain polymer, this film was more easily oxidized; this study was repeated multiple times to verify results, and each time, the $P(OE)_3$-E spectra was that of a partially oxidized rather than fully reduced film. The results from PE and P-E-iI-E serve as confirmation that for these dioxythiophene-based electrochromic polymers, there is not a large difference between the reduced states for films of different thicknesses.

Traditionally, the oxidized state is studied to track changes in transmittance with thickness, as was performed earlier in this study. As demonstrated, the reduced state does not vary significantly, which means that the oxidized state can be a measure of contrast, and Figure 7 can also be used to compare the contrasts of the various families. Figure 8 visualizes this in a simpler format, demonstrating that for PE, the reduced state remains relatively constant despite changes in thickness, but this is not the case for the oxidized state.

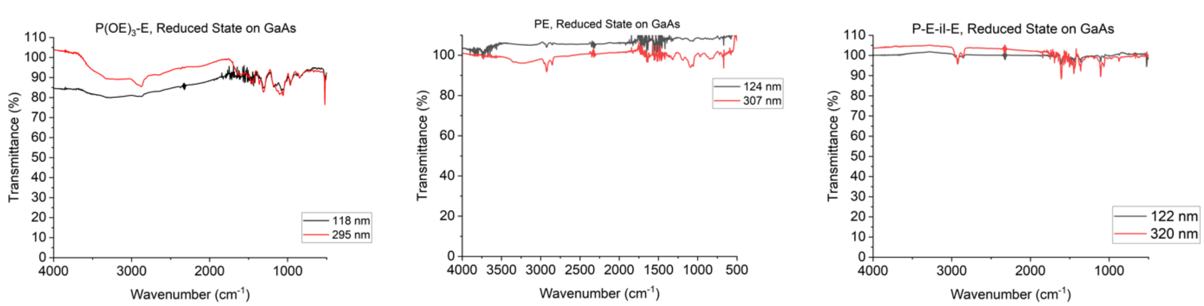

Figure 6. Comparison of the reduced spectra for the three different polymers examined in the structural studies. These films were on gallium arsenide and reduced using hydrazine.

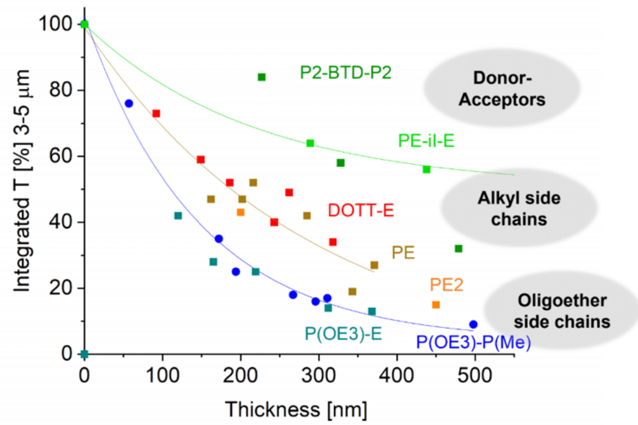

Figure 7. Comparison of transmittances of the oxidized state of various polymers across different thicknesses of film on gallium arsenide.

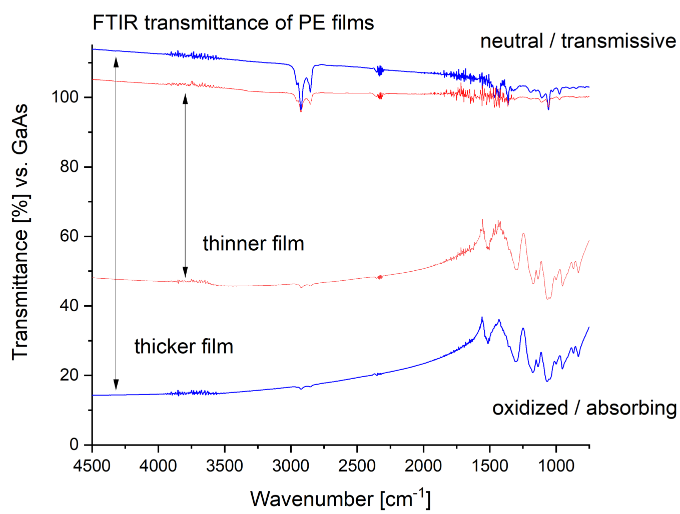

Figure 8. Comparison of neutral states and oxidized states for thinner and thicker films of PE.

3.4: Comparing Donor-Acceptor Polymers in Electrochromic Devices and on Gallium Arsenide

After understanding key properties of donor-acceptor polymers in mid-IR switching electrochromic devices, the specific differences between the two polymers (P-E-iI-E and P(ProDOT$_2$-BTD-ProDOT$_2$)) were studied in prototype devices, allowing for additional identification of their potential success in devices and if there is a significant difference in their IR contrasts. Similarly to before, IR contrasts at different wavenumbers and points in the spectra can be found by subtracting the lowest reflectance from the highest reflectance, thus indicating the percentage of change in the device's reflectance. A higher contrast is a more successful IR switching device. Shown in Figure 9 is the IR contrast of a 263 nm P(ProDOT$_2$-BTD-ProDOT$_2$) electrochromic device, with a photograph of the device in question directly adjacent. This device not only displayed contrast via the quantitative data, where the contrast ranged from 47% to 64% across the 3-5 micron region, but also qualitatively to the eye. While the polymer initially has a distinct visually green color, upon application of higher, positive voltages, this polymeric film gets successfully oxidized and is visibly clear.

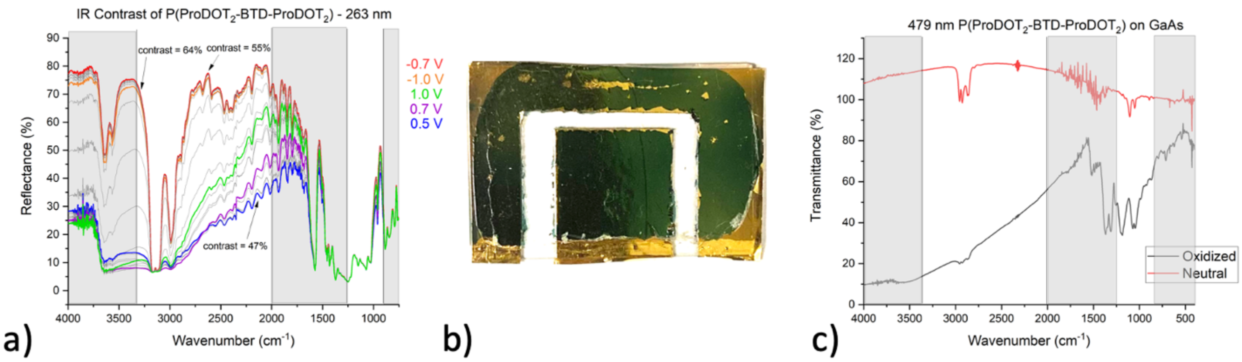

Figure 9. a) IR contrast of a 263 nm thick P(ProDOT$_2$-BTD-ProDOT$_2$) device. b) Example P(ProDOT$_2$-BTD-ProDOT$_2$) electrochromic device, shown in the as sprayed, open circuit state. c) Oxidized vs. neutral spectra of P(ProDOT$_2$-BTD-ProDOT$_2$) on gallium arsenide, graphed as transmittance vs. wavenumber. All spectra are FTIR spectra, highlighted in the 3-5 and 10-12 micron regions (those of interest to IR cameras).

Also displayed in Figure 9 is the differences in transmittance of an oxidized and neutral spectra on gallium arsenide. Note that while electrochromic device data is displayed in terms of reflectance, thin film data is displayed as transmittance. This is because gallium arsenide is highly IR transmissive, making it possible to show transmittance data; the gold Kapton tape used in all electrochromic devices is reflective.

In both the electrochromic device and thin film data for P(ProDOT$_2$-BTD-ProDOT$_2$), the polymer demonstrates excellent and clear contrast. As expected, this contrast is more significant in thin film form, where there is not potential interference from electrolyte. These two different techniques are both successful in measuring and displaying IR switching of a polymer, but the electrochromic device, in which a voltage is applied, is more common in the specific plausible applications of these polymers.

Figure 10 displays similar data but for the other donor-acceptor polymer in this study, P-E-iI-E. The P-E-iI-E electrochromic device, for which the data was selected out of multiple different thicknesses, had contrasts ranging from 22% to 27% across the 3-5 micron region. The displayed data shows the contrasts that are most representative of the series of devices made for each polymer. This contrast is reasonable for the applications and shows great promise for P-E-iI-E as an electrochromic polymer; however, it is significantly less than its other donor-acceptor counterpart. Also displayed in Figure 10 is the thin film (gallium arsenide) data for P-E-iI-E, which also displays successful contrast, despite being significantly less than that for P(ProDOT$_2$-BTD-ProDOT$_2$).

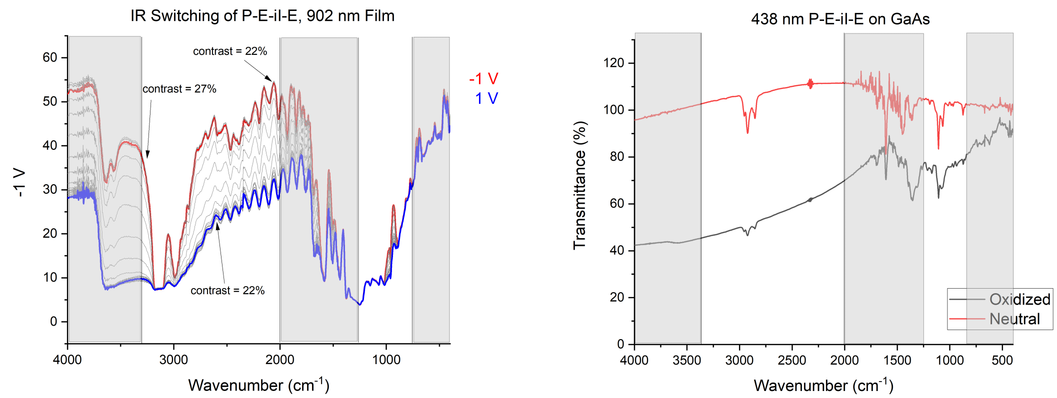

Figure 10. IR contrast of a 902 nm thick P-E-iI-E device (left). Oxidized vs. neutral spectra of P-E-iI-E on gallium arsenide (right). Graphs are highlighted in the 3-5 and 10-12 micron regions (those of interest to IR cameras).

The data collected for these two polymers shows that while either donor-acceptor polymer is a good option for IR switching applications, P(ProDOT$_2$-BTD-ProDOT$_2$) has higher contrast and is the superior candidate of the two.

3.5: Comparing Polymers of Different Structural Groups in Electrochromic Devices

After studying the donor-acceptor series of polymers in depth, the studies progressed to examining specific differences in structural features. The three groups of polymers studied here were alkyl side chain (represented by PE), oligoether side chain (represented by P(OE)$_3$-E), and donor-acceptor (represented by P-E-iI-E). While, as shown above, P(ProDOT$_2$-BTD-ProDOT$_2$) was a donor-acceptor polymer with higher contrast, this polymer was proven to be more difficult to work with. For this examination of structural changes affecting contrast, it was reasonable to use P-E-iI-E.

For the comparisons of the electrochromic devices here, similar thicknesses were selected for each polymer in order to have as direct a comparison as possible. Figure 5 shows the IR contrast of a 305 nm PE device, with 19% contrast. This device had a strong visual switch, also shown in Figure 11, verifying the results and the switching ability of the polymer film upon application of a voltage. The -1 to 1 V voltage range was again used, and this was the range in which the highest device contrast was achieved; extending this voltage range downward did not significantly increase the contrast.

Comparatively, the P-E-iI-E device displays even smaller contrast at 14%; this device had a polymer film thickness of 355 nm, a smaller thickness generating a smaller contrast than the previously studied P-E-iI-E devices. However, this thickness, being comparable to that of the PE electrochromic device, allows for a direct comparison between the two. PE, the polymer with alkyl side chains, had a stronger IR contrast than P-E-iI-E, the donor acceptor polymer.

Additionally shown in Figure 12 is electrochromic data for P(OE)$_3$-E at a thickness of 307 nm, which displays an IR contrast significantly greater than that of either of the other polymers. Visually, a strong drop in reflectance to almost zero is seen as the voltage increases. Additionally, this voltage is seen at only -0.2 V, showing that a smaller operating voltage range can be used for this polymer to the same degree of success. The contrast of P(OE)$_3$-E was 58%; almost 40% better than the other two polymers being studied. The disappearance of strong IR peaks in the 3-5 micron range as the voltage being applied increases also proves impressive properties for this polymer.

Overall, the electrochromic data for the three structurally different polymers shows unique attributes and switching capabilities for each one. The polymer with polar oligoether side chains had the strongest contrast by far, suggesting that the addition of this structural feature has a positive impact on the polymer's electrochromic abilities in the regions of interest, increasing IR contrast by approximately 40%. The polymer with alkyl side chains had the next best contrast, followed by the donor-acceptor polymer, though these were very comparable. This demonstrates that the addition of the alkyl side chain structural feature has a more significant impact on IR switching than the donor-acceptor network featured in P-E-iI-E or P($ProDOT_2$-BTD-$ProDOT_2$).

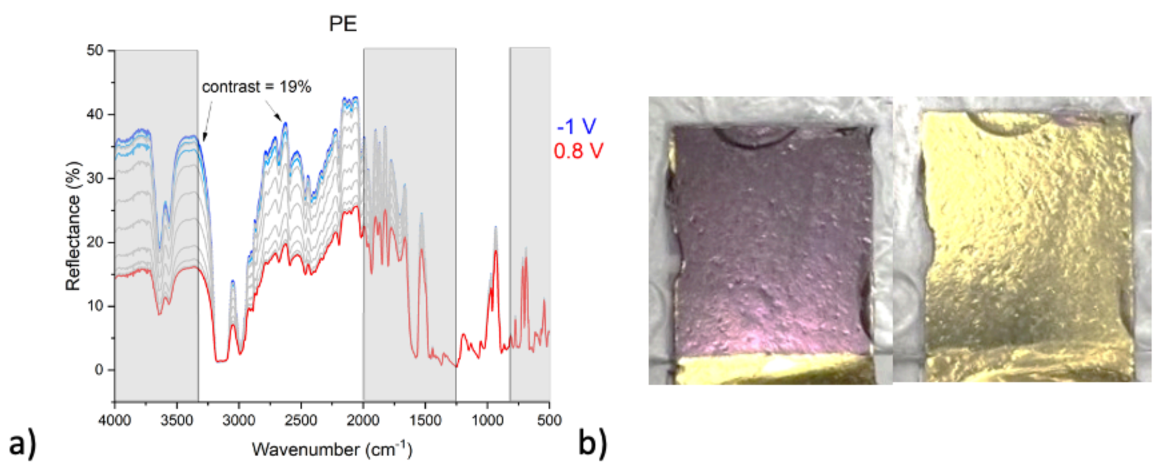

Figure 11. a) IR switching of a 305 PE device along with b) the same device after application of -1 V (left) and 1 V (right).

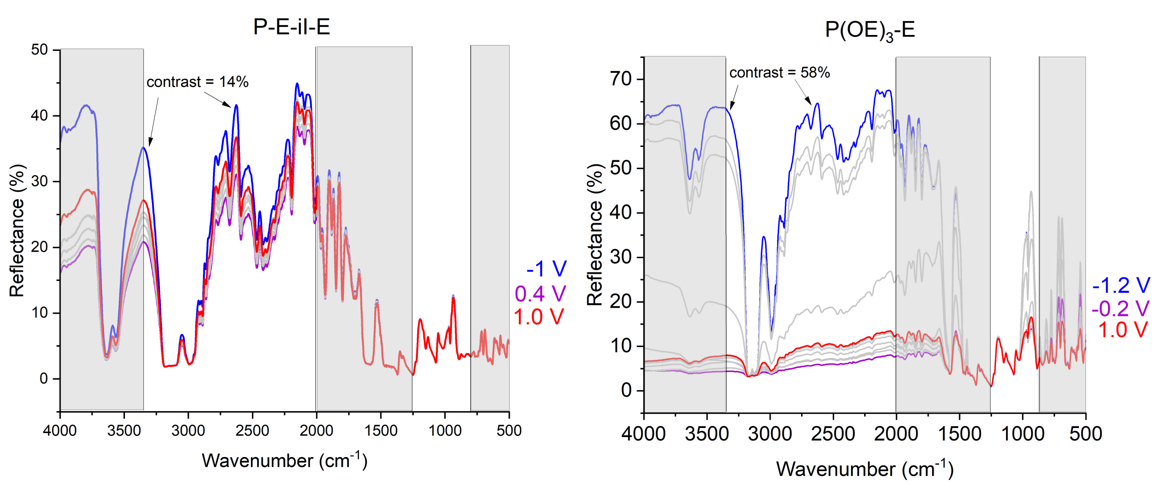

Figure 12. IR switching of P-E-iI-E (left) and $P(OE)_3$-E (right).

Chapter 4: Discussion

4.1: Initial Studies

Prior to the development of concrete data on the IR switching of the series of polymers studied, the key parameter of thickness was optimized for both thin films on gallium arsenide and devices. Utilizing devices with an absorbance of around 1 was ideal; thicker polymer films were successful but challenging to spray to consistent thicknesses, while thinner polymer devices had minimal contrast.

For thin films on gallium arsenide, the comparison of transmittance vs. thickness showed that these two properties have a negative exponential correlation; as thickness increases, transmittance decreases. This follows with what was seen and understood with elementary device studies. However, out of the two donor-acceptor polymers in this part of the study, P-E-iI-E had a much more gradual decrease in transmittance than P(ProDOT$_2$-BTD-ProDOT$_2$). This is not easily attributable to features beyond the slightly larger bulk of the P(ProDOT$_2$-BTD-ProDOT$_2$) polymer, making this polymer more difficult to spray and have generally lower transmittance in accordance to thickness. Despite the differences between these two polymers, the central finding from studying these polymer thin films was that transmittance decreases with an increase in thickness.

Another elementary study was performed on the structurally different polymers PE, P-E-iI-E, and P(OE)$_3$-E. This study aimed to prove that the reduced state of these polymers on gallium arsenide was not thickness dependent and that contrast could be assumed based on the oxidized state, and upon examination of the collected data (Figures 11-12), it is clear that the reduced state is relatively consistent across both thin and thick films for these polymers. This means that the oxidized states can be compared across different thicknesses for thin films of polymers with all of the structural groups in this study without significant regard to the reduced state, as it will remain consistent. Figure 10 demonstrates the preliminary knowledge that the oligoether side chain polymers will have the highest contrast, as these demonstrate the greatest difference between oxidized state transmittance and 100% (the assumed reduced state) for all thicknesses. This finding is additionally important for defending studies such as the previous transmittance vs. thickness study, which was done on the oxidized state, and for setting up future studies examining contrast with a focus on the oxidized state.

4.2: Donor-Acceptor Polymer Comparisons & Studies

Each of the donor-acceptor polymers (that is, P-E-iI-E and P(ProDOT$_2$-BTD-ProDOT$_2$)) were studied for their IR contrast within electrochromic devices (where the film was electrically oxidized and reduced and the output spectra is reflectance) and as thin films (where the film was chemically oxidized and reduced and the output spectra is transmittance). These two methods should yield relatively similar results, with the exception of minor variations occurring due to potential effects of the electrolyte in the reflectance of the film.

The contrast for P(ProDOT$_2$-BTD-ProDOT$_2$) was around 50% in device form; this is excellent contrast for an electrochromic device, with previous studies showing PEDOT to have a contrast of around 15.3% and metal oxide devices to have around 30% modulation.[2] The contrast was even higher when this polymer was studied as a thin film, which makes sense when considering the effects of electrolyte. Overall, the study of both possibilities showed that this polymer can be used successfully in a system where electrically induced oxidation and reduction is required or in an environment where chemical change is preferred. The electrochromic device builds are the most similar to how these polymers would IR switch in real-world applications, making the 50% contrast a great judge of how this polymer would perform.

The contrast for P-E-iI-E was around 25% in device form and 45% in thin film form, proving that this donor-acceptor polymer performed half as well as P(ProDOT$_2$-BTD-ProDOT$_2$). Comparing this to past work on metal oxides, this is still excellent contrast that is almost matching the 30% modulation of those devices.[2] The difference in IR performance for two polymers of the same donor acceptor family is likely due to the acceptor group in the structure; these polymers have the same dioxythiophene-based donor group, so it could be concluded that P(ProDOT$_2$-BTD-ProDOT$_2$)'s acceptor group is more viable for increasing IR contrast. Overall, great developments have been made for these donor-acceptor polymers in terms of IR contrast, and further studies can be performed to continue to optimize the structures of these polymers to yield the best results.

4.3: Structural Group Comparisons & Studies

Studies comparing polymer structural groups were primarily done in device form to mimic performance that would occur in real-world applications; the change in the reflectance of these devices upon the applied potential can be used in many of the previously specified applications, such as thermal camouflage and traffic visualization[1,2]. When examining the IR contrast across 3 structurally different polymers, the oligoether side chain polymer, P(OE)$_3$-E, had the best contrast, followed by the alkyl side chain polymer (PE) and donor-acceptor polymer (P-E-iI-E) respectively. These polymers are structurally similar with minor differences in backbone & side-chain; PE and P-E-iI-E differ only by their side chains and the polarity of their side chains, while P(OE)$_3$-E has a change to the backbone creating a more electron poor structure with donor and acceptor units. The specific IR comparison shows that making one simple change to a dioxythiophene-based conjugated polymer backbone or side chain can have large impacts to the IR switching capabilities.

P(OE)$_3$-E had especially impressive properties, with contrasts of over 50%. This demonstrates that that utilizing oligoether side chain structural features in these polymers contributes greatly to their IR switching success. The study done here is an excellent introductory point to future studies examining the structural features of various electrochromic polymers that affect IR switching, as it proves the success of oligoether, or polar, side chains over other features. Additionally, this study examined other potential polymers that can contribute to advanced knowledge of IR switching; continuing to grow this field is of great interest due to the widespread applications, and it is excellent to see the progress in developing great organic materials for these purposes.

Chapter 5: Conclusion

The electrochromic polymers examined in this study are each promising materials in the infrared region, with the contrast demonstrated by each indicating the potential success of dioxythiophene-based conjugated polymers for IR switching applications. The work here demonstrated how both polymer thin films and devices have IR contrast that is thickness-dependent; this understanding was both crucial to further device development in this work itself and relevant to further study on electrochromic polymers moving forward. Furthermore, donor-acceptor polymers were compared in terms of their acceptor group for increasing contrast; P(ProDOT$_2$-BTD-ProDOT$_2$) was found to be more successful than P-E-iI-E.

The most significant finding of this work was in the comparison of polymers with varied structural groups. Oligoether side chains were found to have the highest contrast, followed by those with alkyl side chains and donor-acceptor polymers. This indicates that polar side chains are crucial to the enhancement of IR contrast and can be employed in dioxythiophene-based conjugated polymers for applications in military camouflage, transportation, and other industries. Future work will be able to focus on other structural features and focus on how to optimize P(OE)$_3$-E individually to have even greater IR contrasts.

Chapter 6: Sources

1. Niu, J.; Wang, Y.; Zou, X.; Tan, Y.; Jia, C.; Weng, X.; Deng, L. Infrared electrochromic materials, devices, and applications. *Applied Materials Today.* **2021**, 24, 101073. DOI: 10.1016/j.apmt.2021.101073

2. Brooke, R.; Mitraka, E.; Sardar, S.; Sandberg, M.; Sawatdee, A.; Berggren, M.; Crispin, X.; Jonsson, M. P. Infrared electrochromic conducting polymer devices. *J. Mater. Chem. C*. **2017,** 5, 5824-5830. DOI: 10.1039/c7tc00257b

3. Sauvet, K.; Sauques, L.; Rougier, A. IR electrochromic WO_3 thin films: from optimization to devices. *Solar Energy Materials & Solar Cells*. **2009**, 93, 2045-2049. DOI: 10.1016/j.solmat.2009.05.003

4. Wang, Z.; Wang, X.; Cong, S.; Geng, F.; Zhao, Z. Fusing electrochromic technology with other advanced technologies: a roadmap for future development. *Materials Science & Engineering R*. **2020**, 140, 100524. DOI: 10.1016/j.mser.2019.100524

5. Cai, G.; Wang, J.; Lee, P. S. Next-generation multifunctional electrochromic devices. *Acc. Chem. Res.* **2016**, *49* (8), 1469-1476. DOI: 10.1021/acs.accounts.6b00183

6. Li, M.; Liu, D.; Cheng, H.; Peng, L.; Zu, M. Manipulating metals for adaptive thermal camouflage. *Sci. Adv.* **2020**, *6* (22), eaba3494. DOI: 10.1126/sciadv.aba3494

7. Tian, Y.; Zhang, X.; Dou, S.; Zhang, L.; Zhang, H.; Lv, H.; Wang, L.; Zhao, J.; Li, Y. A comprehensive study of electrochromic device with variable infrared emissivity based on

polyaniline conducting polymer. *Solar Energy Materials & Solar Cells*. **2017,** 170, 120-126. DOI: 10.1016/j.solmat.2017.05.053

8. Anderson, T.E.; Culver, E. W.; Badía-Domínguez, I.; Wilcox, W. D.; Buysse, C. E.; Delgado, M. C. R.; Rasmussen, S. C. Probing the nature of donor-acceptor effects in conjugated materials: a joint experimental and computational study of model conjugated oligomers. *Phys. Chem. Chem. Phys.* **2021**, 23, 26534-26546. DOI: 10.1039/d1cp04603a

9. Van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. Developments in the chemistry and band gap engineering of donor-acceptor substituted conjugated polymers. *Materials Science & Engineering: R*. **2001**, *32* (1), 1-40. DOI: 10.1016/S0927-796X(00)00029-2

10. Ghosh, R.; Chew, A. R.; Onorato, J.; Pakhnyuk, V.; Luscombe, C. K.; Salleo, A.; Spano, F. C. Spectral signatures and spatial coherence of bound and unbound polarons in P3HT films: theory versus experiment. *J. Phys. Chem. C*. **2018**, 122, 18048-18060. DOI: 10.1021/acs.jpcc.8b03873

11. Enengl, C.; Enengl, S.; Pluczyk, S.; Havlicek, M.; Lapkowski, M.; Neugebauer, H.; Ehrenfreund, E. Doping-induced absorption bands in P3HT: polarons and bipolarons. *ChemPhysChem.* **2016**, 17, 3836-3844. DOI: 10.1002/cphs.201600961

12. Padilla, J.; Österholm, A. M.; Dyer, A. L.; Reynolds, J. R. Process controlled performance for soluble electrochromic polymers. *Solar Energy Materials & Solar Cells*. **2015**, 140, 54-60. DOI: 10.1016/j.solmat.2015.03.018

13. Petroffe, G.; Beouch, L.; Cantin, S.; Aubert, P.; Plesse, C.; Dudon, J.; Vidal, F.; Chevrot, C. Investigations of ionic liquids on the infrared electroreflective properties of poly(3,4-ethylenedioxythiophene). *Solar Energy Materials & Solar Cells.* **2018**, 177, 23-31. DOI: 10.1016/j.solmat.2017.07.018

14. Wu, E. C.; Salamat, C. Z.; León Ruiz, O.; Qu, T.; Kim, A.; Tolbert, S. H.; Schwartz, B.J. Counterion control and the spectral signatures of polarons, coupled polarons, and bipolarons in doped P3HT films. *Adv. Func. Materials.* **2023,** 33, 2213652. DOI: 10.1002/adfm.202213652