ELECTROCHEMICAL GATING OF DOPED POLYMERIC SEMICONDUCTORS WITH HYDROGEN-BONDING SIDE CHAINS

A Dissertation
Presented to
The Academic Faculty

by

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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the
School of Chemical and Biomolecular Engineering

Georgia Institute of Technology
May 2021

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ELECTROCHEMICAL GATING OF DOPED POLYMERIC SEMICONDUCTORS WITH HYDROGEN-BONDING SIDE CHAINS

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To my family,

for whom I am incredibly fortunate
to have their unconditional love and support;

and to my late grandparents,

who instilled in me numerous life lessons.
ACKNOWLEDGEMENTS

My first formal foray into graduate school involved searching for a group that I wanted to be part of—this involved having clear discussions with a few potential advisors and multiple coffee outings with their graduate students. I first met Professor Elsa Reichmanis in her office in September 2016, where we discussed her group’s work in solution processing of organic semiconductors. Elsa is one of the most understanding and incredibly thoughtful mentors that I have had – as an inexperienced graduate student I often encountered nebulous situations that she helped guide me through, for which I owe my deepest gratitude to. I am thankful to have an advisor who offers so many intangibles such as excellent communication, emotional support, and working relationships with her graduate students – I am incredibly lucky to have one of the best advisors any graduate student might possibly want.

I wanted to also thank Professor Natalie Stingelin, who served as my Georgia Tech advisor for my last graduate year when Elsa announced her move to Lehigh University. Natalie graciously accepted me and my fellow labmate, Audrey Scholz, into her group and made both of us feel welcome despite short notice. Natalie is additionally a great mentor that I can rely on to provide transparent and critical feedback for being an excellent scientist – and I thank her for helping take care of Audrey and me near the end of our studies.

I am additionally grateful to Professor Carlos Silva, who played an important role in helping me understand a little bit more of the complex beast that comprises spectroscopy. I wanted to extend my thanks to Professors Sven Behrens and Saad Bhamla for providing
numerous big picture insights and outside perspectives to my work, and for serving as excellent, responsive thesis committee members.

Although not on my committee nor involved with my final work, I wanted to thank Professor Paul Russo for teaching me a great deal about academia and how to critically think about my research, delivered in a lighthearted and sometimes satirical manner. Beyond graduate school, I am also indebted to Professors Blair Brettmann and Will Gutekunst for providing level-headed commentary and advice with regards to the Student Polymer Network—after all, coordinating seminar sessions and encouraging the growth of a polymer community is a joint effort between both students like myself and professors in the soft matter field, and a lot of the success of SPN would not be possible without them.

Throughout graduate school, much of my time in lab or the office was spent with my fellow Reichmanis group members, many of whom are reliable lab colleagues and great friends outside of work. I wanted to provide special thanks to all several past and current members, but especially to the following—Krysten, thanks for initially convincing me to think more about the Reichmanis group and eventually becoming a lab member; Mike, for providing much needed comic relief, entertainment to the office, and all things cleanroom-related; Ping-Hsun, for answering my afternoon or night time questions when I was a first year; Bailey, for being one of my first mentors and role models in graduate school; Zhibo and Carolyn, for helping with experimental planning down to the detail; Audrey, for being an excellent group leader and bringing all of us together for lunch and socials; Miguel, for spontaneously checking on me and everyone else via random phone calls; Caria, for offering candid takes and being a reliable labmate to help out with anything needed; Aaron, for endless dad jokes (like Mike) and bringing professionalism to our office when it’s time
to work; Rahul, for employing the Socratic method (sometimes too consistently) and being a great mentee; and Yulong, for helping me translate the language of spectroscopy and providing general support—thank you all so much.

Along the way, several others have been instrumental in propelling me from high school student to being at the verge of closing out my doctoral degree. These include Letta Meyer, my high school chemistry teacher, who convinced me that chemistry and all things science-related were worthy pursuits; Professor Ana Claudia Arias, for helping jumpstart my initial research career at Cal; and Girish Gopal, my supervisor at Applied Materials, with some choice words about career decision-making and figuring out how to navigate the lines between academia and industry.

Of course, none of this would be possible without the unconditional support of my parents and brother throughout graduate school, and for over the past two decades. A lot of the life lessons and habits still work-in-progress today are developed upon the solid grounding that they provided as I was growing up—and no matter what happens with friends and colleagues over time, I will always have my family to talk to at the end of the day, every day.

Lastly, I wanted to thank all the close friends who have been with me since high school or undergraduate years—I am incredibly fortunate to have friends (in addition to my labmates) who can talk about anything and everything, and this is more evident during times of isolation, as caused by the pandemic.
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LIST OF SYMBOLS AND ABBREVIATIONS

\( C^*_{A} \)  Effective diffusional pseudocapacitance (areal)
\( C^* \)  Effective diffusional pseudocapacitance (volumetric)
\( C_{A,DL} \)  Effective double-layer capacitance (areal)
\( C_{V,DL} \)  Effective double-layer capacitance (volumetric)

CMOS  Complementary metal-oxide-semiconductor

CNT  Carbon nanotubes

DFT  Density functional theory

DPP  Diketopyrrolopyrrole

\( E_{\text{cell}} \)  or \( E \)  Cell electrochemical potential

MOSFET  Metal-oxide semiconductor field-effect transistor

OECT  Organic electrochemical transistor

OFET  Organic field-effect transistor

OLED  Organic light-emitting diode

PEDOT:PSS  Poly(3-4-ethylenedioxythiophene):poly(styrenesulfonate)

PEO  Poly(ethylene oxide)

PProDOT  Poly(3,4-propylenedioxythiophene)

P3AT  Poly(3-alkylthiophene)

P3C(Bu)T  Poly [3-((5-carboxybutyl)thiophene]

P3C(Pe)T  Poly [3-((6-carboxypentyl)thiophene]

P3CPT or P3C(Pr)T  Poly [3-((4-carboxypropyl)thiophene]

P3HT  Poly(3-hexylthiophene)
P3KBT or P3K(Bu)T

Poly(3-(Potassium-4-butanoate)thiophene

$q$  Momentum vector

$q_{xy}$  $x$- or $y$-component of momentum transfer vector

$q_z$  $z$- component of momentum transfer vector

$R_{CT}$  Charge-transfer resistance (areal)

$R_e$  Bulk resistance (equivalent series resistance)

$\tau_D$  Diffusional time constant

$\chi^2$  Goodness-of-fit parameter
SUMMARY

This thesis aims to explore the potential impact of mixed ionic-electronic conductivity resulting from addition of hydrogen-bonding side chains to polymeric semiconductors. This unique functionality enables the direct use of such materials in bioelectronics applications, where ionic-electronic interfaces in hydrated environments are highly desired.

Aim 1 discusses a preliminary work quantifying the mixed conductivity of a carboxylated polythiophene that initially functioned as a polymeric binder for magnetite-based anodes. Aim 2 expands on Aim 1 to quantify the impact of alkyl spacer length on mixed conduction in aqueous systems. Electrochemical studies on these poly[3-(carboxyalkyl)thiophene]s (alkyl spacer length = 3 – 5) indicate that side chain length does not play a significant role in dictating the doping kinetics in aqueous media. Aim 3 moves beyond the simple model polythiophene backbone and examines how ester and carboxylic acid-based side chains impact the aqueous electroactivity of a high mobility donor-acceptor backbone. Compared to their polythiophene counterparts, the functionalized donor-acceptor polymers demonstrated little electroactivity in aqueous media. These contrary results indicate that addition of hydrogen-bonding side chains may play a role in inducing aqueous electroactivity in select polymers, but that chemical structure and further side chain engineering is needed to qualitatively predict whether polymers can be made aqueous electroactive.
CHAPTER 1. INTRODUCTION

1.1 Understanding the role of organic electronics

One cannot possibly imagine how today’s electronics might function without the invention of the first working transistors at Bell Labs in 1947 by Bardeen, Brattain, and Shockley. For the first time, these revolutionary devices demonstrated amplification and rapid on/off switching in a small form factor, supplanting their vacuum tube predecessors. By 1959, a sleeker form of these transistors, known as the metal-oxide-semiconductor field-effect transistor (MOSFET), jumpstarted the miniaturization of electronics that we continue to pursue today. Integrated circuits could be built with ever-increasing MOSFET density, yielding faster performance and lower power consumption. Today, MOSFETs are a fundamental building block for today’s semiconductor devices, responsible for the digital logic powering our personal computers and smartphones. Substantial research and development efforts persist today to continually increase transistor density per integrated circuit to keep up with the ever-increasing demands of information transfer.

In the 21st century, scientists have strived to bring the transformative nature of microelectronics and digital logic to realms that operate over characteristic lengths of millimeters to meters, i.e. macroelectronics. Macroelectronics can be roughly divided into three overlapping categories:

1) **large-area** electronics, where the focus is on large-scale devices with little or no constraints on deformability, such as displays;
(2) **bioelectronics**, to develop devices adept at collecting information in biologically relevant environments, such as biosensors;

(3) **deformable** electronics, which focuses primarily on devices or constructs that can be informally considered “flexible” or “stretchable”, such as electronic skin.

An initial attempt to tackle research problems in these realms would be to directly utilize our decades-extensive expertise in microfabrication involving crystalline silicon and III-V semiconductors. However, CMOS technology does not scale well to area-intensive applications – especially considering several feasibility parameters such as cost or mechanical compliance. Today’s fabrication skillsets cannot solely be used to develop macroscale devices.

This incompatibility can be partly attributed to the main aim of microelectronics – maximizing the density of transistors on a chip while optimizing cost and performance. In macroelectronics, area is no longer a premium; the challenge is to pattern digital logic and functional components over large areas while maintaining the consistency and robustness of their microelectronic counterparts.

The cost for patterning information using different methods can be summarized in Table 1, courtesy of Arias et al. Although these prices are from 2010, the comparison between differing processing methods still hold today.
Table 1 – Cost of Patterning Information over Different Areas (2010 pricing)

<table>
<thead>
<tr>
<th>Technology</th>
<th>Patterning</th>
<th>Cost per bit ($)</th>
<th>Areal cost ($-/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>newspaper</td>
<td>Offset</td>
<td>2 x 10⁻¹⁰</td>
<td>1 x 10⁻⁵</td>
</tr>
<tr>
<td>consumer</td>
<td>Inkjet</td>
<td>5 x 10⁻⁹</td>
<td>1 x 10⁻⁴</td>
</tr>
<tr>
<td>a-Si TFT</td>
<td>3 µm lithography</td>
<td>3 x 10⁻¹⁰</td>
<td>3 x 10⁻²</td>
</tr>
<tr>
<td>MOS-Si</td>
<td>&lt;0.1 µm lithography</td>
<td>1 x 10⁻¹¹</td>
<td>3 x 10⁰</td>
</tr>
</tbody>
</table>

The areal cost for microelectronics technologies is 2-5 orders of magnitude more expensive than newspaper or magazine printing methods, even though all techniques offer similar costs per bit of printed information. This discrepancy comes from the utilization of nanoengineered materials and bespoke miniaturized structures to store higher amounts of information into smaller areas. Consequently, fabrication of macroelectronics solely using current microelectronics paradigms would be prohibitively expensive.

Additionally, many area-intensive applications and/or devices often require some degree of flexibility or stretchability – hereby referred to as deformability. Fabrication of mechanically compliant devices is often difficult in the microelectronics space because many utilized materials are too mechanically “stiff” to accommodate deformation strain, strain-relief structures (serpentine interconnects, pre-fracturing) or ultrathinning must be used. Another issue is the lack of deformable substrates thermally compatible with contemporary microchip manufacturing steps. Even if the highest temperature steps of oxidation and silicidation (700-1050 °C) are ignored, chemical vapor deposition (CVD), atomic layer deposition (ALD), and molecular beam epitaxy (MBE) operate at temperatures well beyond the melting points of candidate plastic substrates. This is not to say that metal or high-melting point substrates cannot be used; rather, this observation...
points out that processes for integrated circuit manufacturing severely limit the number of suitable substrates for mechanically compliant applications.

These reasons are symptomatic of the divide between microelectronics technology and macroelectronics’ overall objective. Consequently, materials beyond silicon, germanium, and III-V semiconductors should be explored to determine if there exist any appropriate materials that are somewhat electronically functional and processable over large areas without extreme areal production costs. Candidate materials suitable to fulfill this niche include solution-processable oxides, nanostructured carbonaceous materials (e.g. nanotubes), and polymeric semiconductors. Common amongst these three classes of materials are solution processability for low-temperature processing (<100 °C) and theoretical electrical mobilities within the ballpark range of standard semiconductors utilized today.

This thesis will primarily focus on polymeric semiconductors as viable platforms for enabling large-area electronics. Because such polymers can be readily solution processed, they act as semiconducting inks that can be printed or sprayed through stencils like newspapers or artwork. In an ideal scenario, combining such active materials with deformable substrates, electrodes, and encapsulation could yield devices that can be inexpensive mass-produced. Proof-of-concept devices using these very constructions have already been demonstrated in the literature; the most prominent include large-area displays\(^5\) (organic light-emitting diodes, OLEDs), flexible solar cells\(^6\), field-effect transistors (OFETs)\(^7\), and soft sensors to couple to biological interfaces\(^8, 9\), although this is not an exhaustive list. Beyond literature, companies such as Sony and Phillips also debuted the first flexible full-color displays utilizing OLEDs in 2007, and today, startups such as
Flexterra (formally known as Polyera) have demonstrated prototypes of wearables with e-ink displays utilizing organic electronics technologies (Figure 1)

Figure 1 – The Polyera Wove Band, a 2016 prototype wearable with an all-flexible display. While promising, the prototype did not enter the market. Photo courtesy of CNN.

Understandably, hype around conjugated polymers has continued to remain prominent today, due to the allure of low-temperature processing. This property enables facile deposition over a variety of form factors, but this convenience comes at a severe cost. Transistors made from polymeric semiconductors suffer from orders of magnitude lower charge carrier mobilities and energy efficiency than state-of-the-art transistors in silicon-based integrated circuits,\textsuperscript{10} illustrated in Table 2.
Table 2 – Performance Metrics Comparisons for Different Materials.10-13

<table>
<thead>
<tr>
<th>Semiconductor Material</th>
<th>Field-Effect Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Cutoff Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon CMOS</td>
<td>$\mu_e \approx 1000$</td>
<td>150 GHz</td>
</tr>
<tr>
<td>Single-walled CNTs</td>
<td>$\mu_e \approx 200$-300</td>
<td>20-60 GHz</td>
</tr>
<tr>
<td>(solution-processed)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal oxides (ZnO)</td>
<td>$\mu_e \approx 20$</td>
<td>5-10 MHz</td>
</tr>
<tr>
<td>Amorphous Si</td>
<td>$\mu_e \approx 1$-10</td>
<td>1 MHz</td>
</tr>
<tr>
<td>OSC</td>
<td>$\mu_e \approx 1$-10</td>
<td>1-20 MHz</td>
</tr>
</tbody>
</table>

Thus, focus on hybrid systems is likely the most palatable trajectory for macroelectronics, retaining the complementary advantages of silicon CMOS with the printability of organic electronics. A potential systems-level implementation of a hybrid electronics interface might consist of a conformable sensing interface fabricated using organic electronics, where signal processing and communication flows through an integrated circuit fabricated using classical microelectronics technology (Figure 2).14

![Figure 2](image)

**Figure 2** – Depiction of a systems-level implementation combining silicon CMOS with printed electronics.
Arguably, the role of organic electronics should focus on opportunities unrealizable via normal silicon CMOS technologies, e.g. sensors, wearables, and displays, with improvements in charge carrier mobility and cutoff frequency a secondary priority.

1.2 The polymeric semiconductor, defined

(Semi)conducting polymers are organic macromolecules whose backbones consist of sp²-hybridized atoms that form alternating single and double bonds. The unhybridized orbitals along the backbone chain connect to form a delocalized pi-system. Due to their conjugation, polymeric semiconductors are also known as conjugated polymers.

The simplest conjugated polymer is polyacetylene, which consists of an unsubstituted conjugated carbon chain. In 1977, Shirakawa, MacDiarmid, and Heeger found that exposure of polyacetylene to halogenic compounds dramatically increased the electrical conductivity by over seven orders of magnitude (10⁻⁵ S-cm⁻¹ to >10² S-cm⁻¹), demonstrating an insulator-metal transition.¹⁵,¹⁶ Today, polyacetylene is not widely used due to its general insolubility, as well its air instability in its conductive form. This initial discovery inspired a flurry of new synthetic efforts to create new polymeric semiconductors which were more processible and stable than this initial polymer (Figure 3). These included new strategies such as adding alkyl side chains to conjugated backbones to improve the solubility in organic solvents.
Figure 3 – Chemical structures of early polymeric semiconductors. (a) (trans-) polyacetylene is the simplest conjugated polymer. (b) Poly(p-phenylene vinylene) was one of the initial polymers popularized in LEDs. (c) Poly(3-hexylthiophene) is a widely studied conjugated polymer with increased solubility.

One might imagine that a series of linear carbon atoms would yield electrical properties akin to graphene, which is an excellent conductor. In an ideal 1D chain, the electronic structure that arises from electronic coupling between adjacent unhybridized p-orbitals is a half-filled pi band, with zero bandgap. However, the alternating single and double bonds characteristic of conjugated polymers results in non-equidistant spacing between adjacent carbons. This structural geometry results in a filled pi-band and an empty pi* band, resulting in semiconducting properties. This electronic structure can be realized by examining how the HOMO and LUMO levels for longer and longer polyenes emerge. (Figure 4) The filled and unfilled bands are also known as the conduction and valence bands, respectively.
The bandgap in polymeric semiconductors is an important parameter that dictates the conductivity character for a given material. For instance, insulators generally have large bandgaps (> 2.5 eV), where electrons from the valence band cannot easily transfer to the conduction band at room temperature. As the bandgap is dictated by the interaction of molecular orbitals along the backbone, synthetic architecture and processing play a large role in controlling emergent electronic properties. In other words, the behavior of the semiconductor is largely dictated by its chemical structure and morphology.

An important consideration when considering the morphology of macromolecular systems is disorder. Polymers are prone to disorder as an inevitable consequence of the numerous conformations energetically available. As weakly bound macromolecules, polymeric semiconductors are especially sensitive to the impact of disorder on their optoelectronic properties. This disorder can stem from differences in polymer chain lengths.
(aka dispersity), inhomogeneous regions of crystallinity, and kinetic trapping stemming from solution processing.

## 1.3 Doping in Polymeric Semiconductors

The term “doping” in polymeric semiconductors is somewhat of a misnomer taken from the inorganic field. In layman’s terms, doping refers to the phenomenon where addition of external species into the semiconductor results in large increases in conductivity. While both inorganic and organic materials can be “doped”, the mechanisms of doping are far from similar.

In inorganic materials, “doping” occurs through atomic substitution. For instance, in silicon, small amounts of arsenic, phosphorus, or boron replace the silicon atoms, making covalent bonds with the host matrix. These elements are Group III or Group V elements, and result in p-type doping (electron deficient, resulting in hole carriers), or n-type doping (electron-rich, resulting in electron carriers). These impurities introduce additional donor/acceptor levels which increases the number of mobile carriers that can conduct electrical current. In p-type doping, acceptor impurities introduce hole levels close to the bottom of the semiconductor bandgap, enabling electrons in the valence band to hop into these levels. This mechanism leaves the valence band with mobile holes, where the number can be modulated through by changing the field with an applied voltage. In n-type doping, donor impurities contribute energy levels close to the top of the semiconductor bandgap, where electrons can be easily excited into the conduction band. These mobile electrons in the conduction band can likewise be tuned with an electric bias. (Figure 5). These new energy levels generated by impurities lie within less than 100 meV of the band edges,
resulting in facile thermal excitation of electrons or holes.\textsuperscript{19} Thus, dramatic changes in conductivities can be realized with impurities in the ppm and ppb ranges.

\textbf{Figure 5} – Band level diagrams of inorganic semiconductors in two different doping states, p-doping (acceptor impurities), and n-doping (donor impurities).

Doping in polymeric semiconductors does not occur through covalent substitution of electron-rich or electron-poor atoms as in inorganics. Instead, electrons must be added or removed from the polymeric system through a myriad of methods, including field-effect doping, chemical doping, and electrochemical doping.

Mechanistic attempts to explain doping in organics falls short compared to inorganics. Hydrogen-like models work extremely well to qualitatively describe the flow of electrons in a doped inorganic system but fall short in describing organic systems. This inability is due to several reasons, listed by Lussem et al.\textsuperscript{20}:
(1) Organic semiconductors have dielectric constants 3-4 times that of inorganics, and since the binding energy scales as the square of the dielectric constant, the binding energies in organics are already an order of magnitude higher.

(2) The effective mass of an organic semiconductor, in both small molecules or polymeric systems, is significantly larger than in inorganics. In other words, the mass per free electron or hole generated in an organic semiconductor is larger than that of an inorganic semiconductor.

(3) Doping in organics does not have simple symmetry of atomic substitution and can often impact the structural geometry of the organic system being doped.

These reasons make doping organic semiconductors more nuanced than that of inorganics. Additionally, practical applications of “doping” in organic semiconductors require doping concentrations in the order of percent, rather than ppm or ppb as in inorganics.\textsuperscript{20}

1.3.1 Field-effect doping

Field-effect doping involves the application of an external voltage bias to shift the band-edges of the organic semiconductor relative to the Fermi levels of metal contacts to extract electrical current. This mechanism is used in OFETs to controllably switch devices on and off by taking advantage of changes in conductivity at the metal-semiconductor interface.

This process usually takes place in an organic field-effect transistor (OFET). An example architecture of a bottom-gate, bottom contact transistor is depicted below. The OFET is composed of three different parts: electrodes, made from electrically conductive
materials with low contact resistance such as gold; the organic semiconductor, which can be the polymeric or small-molecule semiconductors deposited through solution-processing or vacuum processing, respectively; and a dielectric, which is an insulator material that is responsible for inducing a field-effect close to the semiconductor.

![Diagram of a bottom gate, bottom-contact organic field-effect transistor (OFET).](image)

**Figure 6** – Bottom gate, bottom-contact organic field-effect transistor (OFET). The dielectric is responsible for inducing an electric field to dope the semiconductor.

In the field of organic semiconductors, the thin-film organic field-effect transistor is commonly composed with silicon as the gate, coated with silicon dioxide (SiO₂, hundreds of nm thick) as the dielectric. Operation of a field-effect transistor starts with a bias between the surface electrodes (source and drain) and the gate electrode – resulting a potential of $V_G$. Because the gate electrode is capacitively coupled to the semiconductor film through the dielectric, charge is induced in the semiconductor film, resulting in field-effect doping.²¹ This charge is mobile and changes in response to the applied surface electrode bias ($V_{DS} = V_D - V_S$). When enough charge is generated in the polymeric semiconductor by inducing potential at the gate, measurements of how this charge changes with $V_G$ can be monitored at a given surface electrode bias $V_{DS}$. At a critical threshold voltage, the gate bias is sufficient to cause the device to turn on.
OFETs are ubiquitous in the literature because they provide a natural way to measure the charge-carrier mobility of a given deposited material. In OFETs, the current between the surface electrodes is a function of the bias above the threshold voltage, the material properties of the dielectric, the distance between the surface electrodes (channel), and the charge-carrier mobility of the semiconductor. As many of these quantities are easily measured or known prior to completion of the experiment, the mobility can be readily back-calculated.

1.3.2 Molecular doping

A natural strategy to “dope” a semiconductor is to incorporate extrinsic molecules that can remove or add charge. This process can occur through a variety of ways, including addition of electron-rich or electron-deficient molecules (charge-transfer doping), acidic or basic molecules (“protonation” doping), and addition of redox-active molecules (chemical doping).

In charge-transfer doping, molecules such as 2,3,5,6-tetrafluorotetracyanoquinodimethane (F4TCNQ) have energy levels that are staggered relative to the organic semiconductor to ensure charge-transfer occurs. Via electron transfer, polarons are introduced in the host semiconductor material. F4TCNQ has been demonstrated as an effective p-type dopant for P3HT, as the predicted band edge of the LUMO for F4TCNQ is deeper than the HOMO band edge of P3HT.22, 23 (Figure 7)
Figure 7 – (a) Chemical structure of F4TCNQ and P3HT, demonstrating electron transfer. (b) Band diagram demonstrating alignment to encourage electron transfer from the valence band of P3HT to the conduction band of F4TCNQ. Figure from Zhang et al. 24

Chemical doping via the addition of Brønsted acids and bases introduces charge close to the semiconductor backbone via hydrogen ions, where the (de)protonated dopant can be considered a counter-ion to the newly charged backbone to ensure charge neutrality. Another class of chemical dopants involves a more significant change than protonation, where charge transfer occurs in tandem with a redox reaction of the dopant.

A major mechanistic difference between field-effect and molecular doping is the timescales and states involved. In field-effect doping, charge is gradually induced in the semiconductor via the dielectric, but this charge is mobile and fluctuates with the amount of bias applied to the gate electrode. Because charge is introduced indirectly and only at the semiconductor-dielectric interface, the polymer microstructure is not modified in operando. In molecular doping, the polymer’s conductivity is modified in a more permanent way since the dopants cannot be removed once added. Additionally, the presence of chemically interacting dopants has a strong effect on the processing and microstructure of the polymer. For instance, addition of F4TCNQ to P3HT yields films
with rougher morphology, as well as shifts in the lamellar and pi-pi stacking of the polymer due to dopant intercalation.\textsuperscript{25}

### 1.3.3 Electrochemical doping

Electrochemical doping can be considered a convolution of field-effect and molecular doping. In this subset of doping, charge originates from conductive electrodes electrically connected to the polymer. The conductive electrodes are connected to a potentiostat, which applies increased potential to shift the energy of electrons in the electrode. When the energy of electrodes is above the LUMO of a p-channel semiconductor, or below the HOMO of an n-channel semiconductor, electron transfer favorably occurs, rendering the polymer conductive and electrochemically doped. (Figure 8)

![Figure 8](image)

**Figure 8.** Depiction of two different electron-transfer scenarios for doping of ferrocene. (a) Homogeneous electron transfer occurs by addition of molecules where the frontier orbital energy levels are already aligned, leading to likely electron transfer—akin to addition of chemical dopants to organic semiconductors. (b) Heterogeneous electron transfer is achieved via use of an electrode to align the energy levels such that electron transfer occurs. Figure from Elgrishi et al.\textsuperscript{26}

A major advantage of electrochemical doping over other methods is that the doped state of the polymer can be easily controlled by controlling the electrode potential. Similar
to field effect transistors, the conductivity of the semiconductor can be switched ON and OFF in the same system. Unlike field-effect transistors, though, counterions must permeate into the electrode to maintain charge neutrality throughout the film as it is charged and reduced. This phenomenon adds an additional feature absent in field-effect doping – an increased dimension in charge transport.

Because charge is generated within the bulk of the semiconductor, higher degrees of doping are possible for conjugated polymers compared to in OFETs. This style of doping can be interrogated in not only three-electrode setups but also OFET-like geometries, where the dielectric is replaced by an electrolyte. This setup is also known as an organic electrochemical transistor (OECT) and can be used to approximate a materials-dependent quantity that is a convolution of charge-carrier transport and charge storage granted by counter-ion transport. 27 (Figure 9)

Figure 9 – Schematic of an organic electrochemical transistor (OECT). The architecture is like a top-gate bottom contact OFET, except the dielectric is replaced by an electrolyte.
1.4 Reframing polymeric semiconductors for mixed conduction

Coupled in the discussion of doping polymeric semiconductors is the dual transport of multiple charged species. While the contemporary focus of polymeric semiconductors has focused on their electron and hole mobility, many polymeric semiconductors demonstrate some degree of ionic mobility—although the relative magnitude of ionic transport in such semiconductors may be relatively small. In chemical and electrochemical doping, extrinsic charge is transferred to polymers while simultaneous counterion transfer occurs to maintain charge neutrality.

Development of macromolecular systems with high degrees of ionic and electron transport is pivotal to supporting existing and next-generation organic electronics technologies. Example applications where mixed conductors could plausibly be used include, but are not limited to, electrochromic systems, sensors, and electrochemical transistors. (Figure 10). In these applications, high degrees of ionic-electronic coupling are necessary to convert between ionic signals resulting from transient changes in these systems to electrical responses. In electrochromics, the rate of ionic transport provides a maximum threshold for the frequency of switching between doping states; sensors, response time and minimum sensitivity; electrochemical transistors, amplification capability. In many of these systems, processing power on the order of nanoseconds is not a key requirement, as it is in inorganic semiconductors. Rather, response times on the orders of fractions to tens of milliseconds is sufficient for applications such as biomarker sensing. Macromolecular systems possessing mixed conduction also exhibit inexpensive pathways for producing macroelectronics that can be conformable, especially in biological applications that require repeated flexion and stretching.
1.4.1 Can polymeric semiconductors function as mixed conductors?

An essential question that should be considered before diving headfirst into this field is considering whether polymeric semiconductors can truly act as mixed conductors; i.e. their ability to transport ions are similar or greater than that of facilitating holes/electrons. This consideration is prominent because arguably, much of the synthetic effort and physics in polymeric semiconductors until the early 2010s has focused on developing universal rules for process-structure property relationships and identifying key morphologies to target for ideal device operation in OPVs and OFETs. In these applications, (electron/hole) charge carrier mobility has been the key figure of merit in dictating whether synthesized materials are deemed promising candidates, not ionic mobility.

Alongside these efforts have been simultaneous thrusts focused on the electrochemistry of such polymers in organic electrolytes since the 1970s. In fact, many
state-of-the-art polymeric semiconductors are able to electrochemically dope in electrolytes such as propylene carbonate and acetonitrile over wide voltage ranges. This fact is well-supported because reports of new polymeric semiconductors are often subject to cyclic voltammetry to estimate their HOMO and LUMO levels, which requires electrochemical doping of a thin film immersed in organic electrolyte. Thus, the answer to the question “can polymeric semiconductors act as mixed conductors” is likely yes. Regardless, two unanswered questions in this emerging field are (1) what chemical structures and morphologies will encourage simultaneous conductivity, and (2) can polymeric semiconductors act as mixed conductors in aqueous media?

1.4.2 Process-structure-property relations in mixed conductors

A major question in understanding mixed conduction of polymeric semiconductors is determining ideal morphologies, microstructure, and local order required to yield high-performance materials. This question is difficult to answer because based on current improvements in ionic and charge-carrier mobility require seemingly contradictory properties. While local order and crystallinity has been demonstrated to play an important role in improving the charge-carrier mobility in polymeric semiconductors, segmental motion and flexible polymer chains are influential in dictating ionic mobility in polymeric electrolytes. This evidence is corroborated in multiple transport studies of model mixed conductors, where ion penetration and swelling in a semicrystalline polymer preferentially occurs in the amorphous fractions of the film.

To probe these properties, experimental methods must be developed from scratch or appropriated from adjacent fields. Today, methods already exist for measuring decoupled
electron or hole transport, as evidenced by the long history of organic electronics. Likewise, ionic conductivity and transport has been widely studied in polymeric systems, as evidenced by the expansive polymer electrolyte field. However, such systems involve the majority transport of one type of charge carrier, requiring less emphasis on coupled transport. In polymeric semiconductors used for mixed conduction, transport is not easily decoupled; the microstructure and photophysics of semiconductors can be significantly disrupted by mobile ions and solvent molecules. Figure 11 demonstrates the expansive toolbox available for studying these unique materials.

Figure 11 – Techniques and devices for probing local order, microstructure, qualitative morphology in mixed conductors. Figure from Paulsen et al. 35
1.5 Motivation and Outline of Thesis

This thesis focuses on the potential mixed conductivity behavior of a set of model polymer semiconductor backbones functionalized with carboxylic acid side chains, with side chain length as a potential parameter for investigation. In this thesis, a polythiophene and a thiazole-functionalized donor-acceptor polymer were selected as model organic semiconductors for examining these process-structure-property relations.

Chapter 2 discusses a preliminary work quantifying the mixed conductivity of a carboxylated polythiophene that initially functioned as a polymeric binder for magnetite-based anodes in works by fellow colleagues Yo Han Kwon and Krysten Minnici. When appropriated for electrochemical transistors, it was found that acid treatment rendered the polymer solvent-resistant in aqueous and organic media, with volumetric capacitances comparable to state-of-the-art polyelectrolyte materials such as PEDOT:PSS. Chapter 3 expands on this initial study by examining the alkyl spacer length on the mixed conduction behavior of carboxylated polythiophenes. Electrochemical studies on these poly[3-(carboxyalkyl)thiophene]s (alkyl length = 3 – 5) indicate that alkyl spacer side chain length plays a small but not significant role in dictating the charge-storage behavior in aqueous electrolyte, as these polymers demonstrate similar charging behavior and exhibit similar doping kinetics. Chapter 4 moves beyond the simple model polythiophene backbone and examines how addition of ester and carboxylic acid side chains impact the aqueous electroactivity of a high mobility donor-acceptor backbone. Compared to their polythiophene counterparts, the functionalized donor-acceptor polymers demonstrated little electroactivity in aqueous media. These contrary results indicate that addition of hydrogen-bonding side chains may play a role in inducing aqueous electroactivity in select
polymer backbones, but that such trends may not necessarily transfer to other backbone systems. Chapter 5 summarizes the main findings in each chapter and provides directions for future research, including in situ microstructural studies monitoring electrochemical doping and blending of carboxylated polythiophenes with commodity polymers such as PEO.
CHAPTER 2. CARBOXYLIC ACID FUNCTIONALIZATION YIELDS SOLVENT-RESISTANT ORGANIC ELECTROCHEMICAL TRANSISTORS

2.1 Introduction

The organic electrochemical transistor (OECT) has been recently revived as a champion platform for multiple applications, including chemical/ion sensing\textsuperscript{36-41}, biological interfacing\textsuperscript{28, 42-44}, and neuromorphic computing\textsuperscript{45-47}. OECTs demonstrate several desirable features, such as low voltage switching, potential for aqueous and biological compatibility, high transconductance, and form factor versatility. Even with an increasing number of viable OECT applications demonstrated in the literature, fundamental understanding of charge transport, ion injection, and structure-property interrelations in electrochemical transistors is primarily limited to extrapolations from commercially available poly(3-4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)\textsuperscript{48-55}. Within the last three years, preliminary studies have also been conducted on potential model materials, such as the “fruit-fly” polymer in field-effect transistors, poly(3-hexylthiophene) (P3HT) \textsuperscript{34, 56, 57}, and one of the highest-performing OECT materials, poly(2-(3,3′-bis(2-(2-(2-methoxyethoxy)ethoxy)-ethoxy)-[2,2′-bithiophen]-5-yl)thieno[3,2-b] thiophene) p(g2T-TT)\textsuperscript{58, 59}, a p-channel thiophene-based polymer with glycolated chains. The success of p(g2T-TT) and other glycolated analogues has highlighted the importance of the side chain chemistry in dictating aqueous electroactivity and increased ability to store charge in bulk. In this work, we demonstrate an alkylthiophene with carboxylic acid derived side chains for OECTs, poly [3-(4-
carboxypropyl)thiophene] (P3CPT), which offers three main advantages: (1) facile film casting from water-soluble carboxylate salt precursors, (2) solvent-resistant films for robust functionality, and (3) dual device functionality in organic and aqueous media. This study opens a path for carboxylic acid functionalized conjugated polymers as useful, accessible, and processable materials for organic electrochemical transistors.

Contemporary OECT materials design revolves around leveraging known high electron/hole mobility backbones and replacing their alkyl chains with alternative moieties to promote aqueous ion transport. Thus far, two principal approaches include the addition of nonionic side chains, especially glycolated side chains, or the addition of ionic side chain functionalities to form conjugated polyelectrolytes. Both methods have historically demonstrated success in appropriating π-conjugated backbones for aqueous ionic transport. In 1990, Roncali et al. demonstrated that introduction of glycolated side chains instead of alkyl side chains resulted in aqueous electroactivity of a simple polythiophene, while redox behavior in organic electrolytes was maintained.60 This synthetic strategy has been utilized effectively to produce functional OECT materials using conjugated backbones such as poly(propylenedioxy-thiophene) (PProDOT),61 polythiophene,34 and donor-acceptor backbones incorporating the n-channel naphthalene diimide-bithiophene unit.62 The second approach aims to improve aqueous ion transport by covalent attachment of ionic moieties to the conjugated backbone. In 1991, water-soluble conducting polymers, specifically sulfonic-acid substituted polythiophenes, exhibited improved doping kinetics as compared to their alkyl counterparts, as charge injection could be easily compensated by cation migration.63 The first conjugated polyelectrolyte directly used for an OECT was reported in 2014, which consisted of a polythiophene with hexanesulfonate side chains.64
More recently, conjugated polyelectrolytes based upon PEDOT-like backbones and blends of PEDOT with polythiophene-based conjugated polyelectrolytes have also been reported.65-68

Frequently, polymers developed with these strategies exhibit significant processing drawbacks. Except for a few backbones such as PProDOT, attachment of hydrophilic side chains to hydrophobic backbones results in low solubility in organic and aqueous solvents. As a result, the synthesis, characterization, and high-throughput processing of such amphiphilic materials becomes much more difficult compared to their alkyl counterparts. On the other hand, water-soluble conjugated polyelectrolytes require cross-linkers to prevent films from dispersing or dissolving in aqueous electrolytes. Thus, a critical gap in the OECT field is the lack of additive-free, highly processable polymer systems. In this context, carboxylic acid functionalized polymers may provide for attractive material platforms. Such polymers have been successfully cast from water-processable precursors to produce solvent-resistant films with notable dual electroactivity in aqueous and organic electrolytes.69-72

Additionally, semiconducting polymers functionalized with carboxylic acid side chains have previously demonstrated bulk electrochemical doping in electrolyte-gated organic transistors, while their alkyl counterparts only exhibit fast interfacial doping.73 Increasing the fraction of carboxylic acid functionalized monomers in a P3HT-based copolymer has been shown to increase the areal capacitance from 21 \( \mu \text{C-cm}^{-2} \) to 380 \( \mu \text{C-cm}^{-2} \), which further indicates that the mechanism of charge storage is not confined to the interface.74 Thus, inclusion of carboxylic acid side chains can fundamentally change the mode of charge storage and transport in polymer films.
2.2 Experimental Methods

2.2.1 Materials

P3KBT (Poly(3-(Potassium-4-butanoate)thiophene-2,5-diyl), \(M_w = 21 \text{ kDa}, \text{PDI} = 2.2, \text{RR}=89\%\)) was purchased from Rieke Metals Inc. \(p\)-Toluenesulfonic acid monohydrate (\(p\)TsOH-H\(_2\)O, 98\%, Sigma-Aldrich), sodium chloride (99.9\%, biotechnology grade, VWR), acetone, methanol, and isopropanol were used as received. Tetrabutylammonium hexafluorophosphate was recrystallized in hot ethanol prior to use. Millipore-processed deionized (DI) water was used with a resistivity of 18.2 M\(\Omega\)-cm.

2.2.2 Film Preparation for Electrochemical and Transistor Measurements

Conjugated polyelectrolyte precursor solutions were dissolved in water at a concentration of 2 mg-mL\(^{-1}\) and stirred at room temperature overnight to ensure complete dissolution. The polymer solutions were spray-cast (Iwata-Eclipse HP-BC Airbrush, 40 psi N2) onto substrates heated to 100 °C. The spray-cast films were converted into their solvent-resistant acid form by dip-coating in 0.1 M \(p\)TsOH-H\(_2\)O in methanol for 10 minutes, rinsing of the film in copious methanol to remove any excess \(p\)TsOH-H\(_2\)O, and subsequent drying under N\(_2\) at 50 °C for 1 hr prior to any electrochemical and spectroscopic measurements.

2.2.3 Isolation of Solvent-Resistant Polymer (for Thermal Analysis)

25 mg of P3KBT was dissolved into 50 mL of deionized water and heated to approximately 50 °C for 20 minutes to fully dissolve the polymer. Then, 400 mg of \(p\)-toluenesulfonic acid monohydrate was added to protonate the carboxylate salt. The desired
carboxylic-acid substituted polymer immediately precipitated out of solution to form dark purple aggregates. The mixture was stirred vigorously for an additional 20 minutes to ensure protonation was complete. The mixture was filtered using a 0.45 µm nylon syringe filter and rinsed with copious amounts of water to remove any trace amounts of P3KBT, followed by methanol to remove the \( p \)-toluene sulfonic acid monohydrate. The resulting solvent-resistant poly [\( 3-(4\text{-carboxypropyl}) \text{thiophene} \)] (P3CPT) was dried under vacuum for 15 hours, affording 12 mg of isolated P3CPT.

### 2.2.4 Cyclic Voltammetry

Cyclic voltammetry was performed using a Gamry Reference 3000 Potentiostat/Galvanostat using a three-electrode setup. The working electrode consisted of spray-coated polymer film on ITO-coated glass slides (Delta Technologies, resistivity = 8–12 Ω sq\(^{-1}\)) and the counter electrode was a stainless-steel plate. For aqueous testing, the reference electrode was a standard Ag/AgCl reference electrode (3M aqueous NaCl inner solution, BASi), with the electrolyte being 0.1 M NaCl in DI water. For organic testing, the reference electrode was an Ag/Ag\(^+\) electrode made in-house. This pseudoreference consisted of an Ag wire suspended in 0.5 M AgNO\(_3\)/acetonitrile and was calibrated as 95 mV vs the ferrocene/ferrocenium redox couple. The organic electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate in propylene carbonate. All electrolytes were degassed with argon flow for 15 minutes prior to and during measurement. Scans were recorded at a scan rate of 50 mV s\(^{-1}\), with a step size of 2 mV.

### 2.2.5 Differential Pulse Voltammetry
Differential pulse voltammetry was performed using the same setup as in cyclic voltammetry. A 20 mV pulse was applied, with an integration time of 50 milliseconds and a step size of 1 mV.

2.2.6 Differential Scanning Calorimetry (DSC)

Flow rate of N₂ was set to 80 mL-min⁻¹. All measurements were carried out with a Mettler Toledo DSC instrument operating under N₂ atmosphere. Polymer samples weighing about 5 mg enclosed in Al pans were used for traces and cycled between -70/-90 °C to 250 °C/300°C at 10 °C-min⁻¹ ramp for three heat-cool cycles.

2.2.7 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy was performed using the same three-electrode setup as described before, with a 10-mV amplitude, scanning between 0.1 Hz and 100 kHz. The working electrode was first conditioned at the probed DC voltage for 60 seconds to ensure film characteristics reached steady-state in order to set the doping level prior to application of the 10 mV AC perturbation.

The fitted resistances \( R_e, R_{CT} \), capacitances \( C_{dl}, C^* \), and diffusion parameters \( Z_W, \pi \) of the P3CPT impedance spectra (in 0.1M NaCl/H₂O) were modeled as a function of applied potential. The equivalent electrical circuit used is shown below.
In the text the pseudocapacitance is referred to as $C^*$, in accordance with other works in this area. Circuit fitting was performed using constant-phase elements for $C_{dl}$, $C^*$ due to the heterogeneity of charge transport in the film, as well as variable film thickness and then converted to an effective capacitance using the following formula:\textsuperscript{75}

$$C_{eff} = \frac{1}{Q^n} R_e \frac{1-n}{n}$$

### 2.2.8 Profilometry

The thickness of P3CPT films were measured using a Dektak XT profilometer. An average was taken for three measurements on different spots.

### 2.2.9 Spectroelectrochemistry

The \textit{in situ} spectroelectrochemical analyses were performed using an Agilent Cary 5000 spectrophotometer in quartz cuvettes (1 cm path length). The working electrode consisted of ITO-coated glass slides (Delta Technologies, resistivity = 8–12 $\Omega$ sq\textsuperscript{-1}) coated in the solvent-resistant form of the polymer, and a platinum flag was used as the counter electrode. An Ag/AgCl reference electrode (3M aqueous NaCl inner solution, BASi) was used to complete the three-electrode cell. The electrolyte consisted of a 0.1 M NaCl
(99.9%, biotechnology grade, VWR) solution in Millipore water. Prior to recording spectra, the film was electrochemically conditioned by performing 20 cyclic voltammetric scans between -0.5 V and +0.9 V vs. Ag/AgCl with a scan rate of 50 mV s$^{-1}$ to ensure reproducibility of the redox characteristics of the polymer. After conditioning, the film was biased under potentiostatic conditions in 100 mV steps, starting with the most cathodic potential and progressively biasing toward anodic conditions. Film spectra were recorded under potentiostatic conditions once the working electrode current had reached a steady-state (~30-60 seconds per 100 mV step).

2.2.10 Transistor Characterization

Interdigitated electrodes were purchased from MicruX Technologies (Model ED-IDE1-Pt, total area = 38.5 mm$^2$, 90 pairs, 10 µm electrode length, 10 µm electrode gap, $d$ = 140-190 nm). Polymer films were spray-cast to approximately 200 nm and converted to solvent-resistant form as previously mentioned. An in-house chloridized Ag wire (Ag/AgCl) was used as the gate electrode, with the films submerged in a 0.1 M NaCl electrolyte solution to form the electrochemical transistor. OECT electrical properties were investigated in ambient atmosphere using an Agilent 4155C semiconductor parameter analyzer. The transistors were held at a de-doping gate voltage ($V_{GS} = -0.1$ V) for 30 seconds to pre-condition the films to an undoped state. The maximum transconductance $g_M$ was calculated in the low-frequency regime (scan rate = 100 mV-s$^{-1}$) from transfer plots of drain current ($I_{DS}$) versus gate voltage ($V_{GS}$) at a fixed drain voltage $V_{DS}$ of -0.6 V using the following equation:

$$g_M = \frac{dI_{DS}}{dV_{GS}}$$
The turn-on behavior was also calculated from output plots by varying $V_{DS}$ from 0.0 V to -0.6 V for gate voltages of 0.0 – -0.8 V in 0.1 V increments.

2.2.11 Thermogravimetric Analysis (TGA)

Flow rate of N$_2$ was set to 80 mL min$^{-1}$. All measurements were carried out with a Mettler Toledo TGA instrument operating under N$_2$ atmosphere. Alumina crucibles were thoroughly cleaned using a butane torch prior to sample loading. 5.1 mg of P3KBT and 4.3 mg of P3CPT was loaded into crucibles and heated from 25 ℃ to 600 ℃ at 10 ℃ min$^{-1}$ ramp, with 2 minutes of initial equilibration at 25 ℃.

2.2.12 X-ray Photoelectron Spectroscopy (XPS)

All measurements were carried out with a Thermo Scientific K-alpha XPS under ultra-high vacuum. The instrument was equipped with a monochromatic Al-K X-ray source (1468 eV). Spectra were collected using an Ar flood gun and a spot size of 400 µm. Survey scans ($n=2$) were collected with pass energy of 146 eV with 1 eV increments. XPS was conducted on polymer deposited on Si substrates cut from single-side polished wafers (N/As doped, 525±25 µm, Rogue Valley Microdevices). Oxygen, carbon, and potassium spectra scans ($n =$10) were also collected in 0.1 eV increments.

2.3 Results and Discussion

2.3.1 Routine Characterization – Protonation and Thermal Stability

Because carboxylic acid functionalized conjugated polymers demonstrate excellent processability characteristics, electrochemical doping, and solvent-resistant properties,
they serve as an emerging class of active OECT materials. As proof of concept, poly(3-(potassium-4-butanoate)-thiophene-2,5-diy) (P3KBT, M_w=21 kDa, PDI=2.2, RR=89%) was spray cast from water to afford thin films on electrodes, and subsequently acidified in a para-toluenesulfonic acid/methanol solution to produce the solvent-resistant poly [3-(4-carboxypropyl)thiophene] (P3CPT) for electrochemical and device testing. (Figure 13).

**Figure 13** – Acidification Scheme for protonation of P3KBT films to form the solvent-resistant P3CPT.

K-to-H protonation was verified through X-ray photoelectron spectroscopy (XPS) of the films before and after treatment. (Figure 14) XPS spectra were collected on spray-cast thin films deposited on Si substrates. The disappearance of the split K2p peaks can be seen in the 290-300 eV binding range, indicating that within the probed cross-section, potassium is completely exchanged. Additionally, increased binding energies in the O1s peak and C1s peak corresponding to the C=O stretch further suggest electron charge is withdrawn from the outer valence electrons, likely due to protonation. During acidification, delamination was also not observed. Combined with the XPS data, it is likely that protonation occurs throughout the bulk of the film.
Comparisons of the solvent-resistant polymer P3CPT demonstrated moderate thermal stability, with a 5% weight loss occurring at temperatures higher than 250 °C, while the water-soluble polymer P3KBT had a characteristic weight loss at 100 °C, presumably due to the presence of water, but thermal stability up to 400 °C. Both polymers degraded at 400 °C, likely due to decomposition of the polymer backbone (Figure 15). To examine potential phase transitions occurring during protonation, differential scanning calorimetry (DSC) was conducted on both polymers. The first heating and cooling cycles are examined to probe for any characteristic peaks prior to melting (Figure 16), while the third heating and cooling cycles are provided to demonstrate the film’s thermal transitions from the melt state (Figure 17). In the initial cycle, the water-soluble P3K(Bu)T precursor

Figure 14 – XPS elemental spectra for oxygen, potassium, and carbon in P3KBT and P3CPT thin films.
exhibits a large endothermic peak centered around 100 °C. This peak can be attributed to the loss of water, as evidenced by the concomitant loss of weight from TGA at 100 °C. Additionally, a broad endothermic peak at 228 °C is observed, although this peak disappears in subsequent cycles. This could plausibly be a melting peak, but no crystallization peak is observed on cooling. For the carboxylic acid polymer P3C(Pr)T, the water peak is not present, but instead another broad peak centered at 80 °C, with a slight shoulder at 206 °C. Like the water-soluble polymer, this higher-temperature peak is not accompanied by another peak in the subsequent cooling cycle.

Figure 15 – Thermogravimetric analysis on P3CPT and P3KBT, run at 10 °C-min-1 ramp.
Figure 16 – Differential scanning calorimetry on the first cycle of P3K(Bu)T and P3C(Pr)T.

Figure 17 – Differential scanning calorimetry (DSC) trace on P3KBT and P3CPT. The third heating and cooling cycles are plotted.

2.3.2 Electrochemical Characterization
To determine the electroactivity of P3CPT, thin film cyclic voltammetry was conducted in a 0.1 M NaCl solution as the aqueous electrolyte and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in propylene carbonate as the organic electrolyte. (Figure 18).

**Figure 18** – Cyclic voltammograms for P3CPT on ITO/glass electrodes in 0.1 M NaCl /H₂O and 0.1 M TBAPF₆/PC at 50 mV-s⁻¹.
Examination of Figure 18 demonstrates that carboxylic acid functionalization enables reversible unipolar p-channel doping in both aqueous and organic electrolytes. The cyclic voltammogram in aqueous solution, conducted at a scan rate of 50 mV-s\(^{-1}\), presents one unique oxidation peak at +0.5 V \textit{vs.} Ag/AgCl, followed by reduction on the cathodic scan at +0.4 V. The increased current density around +0.6 V is caused by the oxidation of water, which limits the voltage window as known for aqueous media. Analogous measurements in the organic electrolyte confirm that the redox process occurs with higher peak current density than in aqueous media, +0.5 V \textit{vs.} Fc/Fc\(^+\), followed by the analogous reduction at +0.3 V \textit{vs.} Fc/Fc\(^+\). In addition, the higher operating voltage window of the organic solvent means that the film can be further oxidized beyond aqueous limits. Differential pulse voltammetry (Figure 19, Figure 20) was also performed on P3CPT films to accurately estimate the oxidation onsets as -23 mV and -470 mV \textit{vs.} Ag/AgCl and Fc/Fc\(^+\) couples, respectively.

**Figure 19** – DPV scan for P3CPT in 0.1 M NaCl in H2O. The measured onset is -23 mV \textit{vs.} the Ag/AgCl couple.
The aqueous and organic voltammograms can be superimposed by aligning their references to the normal hydrogen electrode (NHE). Here, it is assumed that the Fc/Fc\(^+\) potential is +0.63 V vs. NHE\(^\text{76}\) and the standard potential for Ag/AgCl is +0.21 V vs. NHE\(^\text{77}\). Overlays of these voltammograms clearly show that redox processes for the organic film occur at higher potentials than in aqueous solutions; this discrepancy is likely due to differences in electrolyte properties, such as ion-polymer interactions, doping anion solvation energies, dielectric constant, and viscosity. Similar differences in the oxidation potential as measured in aqueous and organic electrolytes have previously been shown for a PProDOT-based material\(^\text{61}\).

Figure 20 – DPV scan for P3CPT in 0.1 M TBAPF\(_6\) in propylene carbonate. The measured onset is -474 mV vs. the Fc/Fc\(^+\) couple.
Figure 21 – Peak current as a function of scan rate for P3CPT in organic and aqueous electrolytes. Values are averaged from three spray-cast film measurements. Dashed lines illustrate extrapolated linear fit for first three points (organic) or four points (aqueous). Error bars represent one standard deviation from the mean.

To probe the kinetics of ion injection in P3CPT, the peak currents of the cyclic voltammograms are plotted as a function of scan rate. (Figure 21) If the resistance between the polymer film and the electrode is assumed to be negligible, this methodology allows us to estimate the speed of redox processes associated with ion migration. At high scan rates, deviations from linearity are likely attributed to ionic transport phenomena. Furthermore, because the polymer films are uniform and relatively thin (140-190 nm), it is unlikely that deviations in linear scaling are due to heterogeneity within the film. The peak current density of P3CPT maintains a linear dependence in aqueous electrolyte up to 500 mV-s⁻¹ and in the organic electrolyte up to scan rates of 100 mV-s⁻¹, respectively. Such a linear
dependence implies that charge carrier kinetics is the rate-determining step at low frequencies, rather than ion diffusion. Thus, this material is estimated to dope (500 mV voltage window) in < 1 s for aqueous electrolyte and 5 s for organic electrolyte. Such doping processes are quasi-reversible; when the scan rates of these films are varied between 10 – 100 mV-s\(^{-1}\), the voltammograms show that increases in scan rate result in slight shifts of the peak potential but maintain similar shapes (Figure 22). Above 100 mV-s\(^{-1}\), the voltammograms ultimately lose peak resolution, indicating the redox processes in these films approach mass transfer limitations.

![Figure 22](image.png)

**Figure 22** – Left: overlaid voltammograms for P3CPT in 0.1 M NaCl in H\(_2\)O for scan rates 20, 50, 100, and 250 mV-s\(^{-1}\). Right: overlaid voltammograms for P3CPT in 0.1 M TBAPF\(_6\) in propylene carbonate for scan rates 20, 50, and 100 mV-s\(^{-1}\).

### 2.3.3 Spectroelectrochemistry

To monitor the optical changes associated with the formation of charge carriers, thin film spectroelectrochemistry measurements were conducted in the aqueous electrolyte. Thin films of P3KBT were sprayed onto ITO-coated glass slides starting from a 2 mg-mL\(^{-1}\) aqueous solution and subsequently acid treated as described above. The solvent-resistant films of P3CPT were submerged in a 0.1 M NaCl solution, and subsequently oxidized using
a stepwise increase in voltage from 0.0 V to 0.9 V \textit{vs.} Ag/AgCl. Gradual evolution of the polaronic/bipolaronic peaks is apparent around 810 nm (1.53 eV) and >1300 nm (<0.89 eV). This evolution occurs with concomitant depletion of the $\pi-\pi^*$ transition at 514 nm (2.42 eV), which is consistent with reports of $\pi-\pi^*$ transitions in polythiophenes functionalized with carboxylic acids.\textsuperscript{78} (Figure 23).

\textbf{Figure 23} – Spectroelectrochemistry of P3CPT in degassed 0.1 M NaCl/H\textsubscript{2}O, with potentials reported \textit{vs.} Ag/AgCl. P3CPT films were also cycled between -0.2 V and 0.6 V for 30 cycles until steady state was reached for the spectroelectrochemistry measurement.

When the absorbance values at these two wavelengths are plotted as a function of applied electrochemical potential (Figure 24), the onset of spectral evolution (-0.1-0.0 V \textit{vs.} Ag/AgCl) is consistent with the onset measured by differential pulse voltammetry (-23 mV \textit{vs.} Ag/AgCl). In addition, the presence of an isosbestic point at 600 nm further suggests that the polythiophene undergoes oxidative doping and that no secondary
processes of different stoichiometry occur within this potential range. P3CPT also exhibits irreversible oxidation at voltages greater than +0.8 V, as evidenced by the simultaneous decrease in the charge carrier bands and $\pi-\pi^*$ transition.

![Figure 24](image)

**Figure 24** – Absorbance at 514 nm (2.41 eV) for the $\pi-\pi^*$ transition and 810 nm (1.53 eV) for the polaronic transition, plotted as a function of potential.

### 2.3.4 Electrical Impedance Spectroscopy (EIS)

We further demonstrate that P3CPT exhibits relatively high pseudocapacitance compared to alternative conjugated polyelectrolytes, which indicates its propensity for storing charges in bulk. It is important to note multiple pseudocapacitance values from OECT literature have used the capacitance value derived from low-frequency fits of simple RC equivalent circuits, which assume an ideal capacitive charging approximation. However, the charging behavior of model conjugated polymer – polyelectrolyte blends such as PEDOT:PSS do not always follow this approximation. It is more accurate to
break down the overall capacitance as a non-faradaic, double-layer contribution and a faradaic, pseudocapacitive contribution. To separate these quantities, electrochemical impedance spectroscopy (EIS) was used to measure the impedance response of P3CPT films in 0.1 M NaCl/H2O. Instead of the commonly used RC circuit, a diffusion-modified Randles circuit is adopted (Figure 12), which has been used to model electrochemically-doped conjugated polymer thin films.\(^{81}\) In this circuit, the electrolyte resistance \(R_e\) is combined with a double-layer capacitance \(C_{DL}\) in parallel with a series combination of the charge-transfer resistance \(R_{CT}\), a finite-length Warburg element, and the pseudocapacitance \(C^*\), and tabulated for three different films. These values are tabulated in Appendix A (Table 5, Table 6, Table 7).

It is especially instructive to quantify the double-layer and pseudocapacitance as a function of oxidation state as extracted from EIS. The double-layer capacitance \(C_{DL}\) roughly increases with oxidation state, which is an observed trend seen in functionalized PProDOTs, and attributed to an increase in accessible interfacial surface area as films swell to accommodate solvated/injected ions.\(^{82}\) Specifically, P3CPT shows an increase in double-layer capacitance by a factor of 3 (Figure 25), as compared to n-octyl-functionalized and tetraester-functionalized PProDOTs, which exhibit an increase by a factor of 8 and 10, respectively.\(^{82}\) This discrepancy suggests that oxidation-induced morphological changes in P3CPT are not as extensive as those associated with the PProDOT systems, likely because the PProDOT system is doped to a higher extent based on spectroelectrochemical data. The pseudocapacitance corresponds to volumetric doping of the film and directly probes the ability of a material to store charge during oxidation state changes. In the aqueous electrolyte, P3CPT exhibits a maximal pseudocapacitance
of $C^* = 150 \pm 18 \text{ F-cm}^{-3}$ at +0.4 V vs. Ag/AgCl (Figure 26). Initially, the increase in applied potential causes the film to swell due to interchain repulsion between charged polymer chains. As the polymer swells, repulsions between positive charges separate the polymer chains, enabling ions and solvent to be more easily incorporated into the film, which increases the pseudocapacitance. As the applied potential increases, the film saturates with charge, which lowers the charge mobility along polymer chains. Charge saturation reduces the proportion of reversible, mobile charges; a combination of charge saturation and decreased mobility ultimately lowers the measured pseudocapacitance at high oxidation states (>0.4 V vs. Ag/AgCl).

**Figure 25** – Calculated double-layer capacitance values for P3CPT films in 0.1 M NaCl/H$_2$O. Values are averaged from three spray-cast film measurements.
2.3.5 Organic Electrochemical Transistor (OECT) Measurements

Based on the oxidation-induced increase in electroactivity, pseudocapacitance, and polaron formation in aqueous media, P3CPT can be utilized as an effective p-channel material for OECTs. P3CPT was deposited on interdigitated electrodes (total area = 38.5 mm$^2$, 90 pairs, 10 µm electrode length, 10 µm electrode gap, $d = 140$-190 nm). Figure 27A and B present typical transfer and output curves for P3CPT-based OECTs. Application of a negative gate bias induces migration of sodium cations to the gate, while chloride anions migrate to the electrolyte/polymer interface. An increase in $|V_G|$ is associated with anion injection into the organic semiconductor film, volumetric bulk doping, and an increase in the source-drain current $I_{DS}$, which is consistent with accumulation-mode operation. A slight hysteresis is observed in the transfer curve when the gate voltage is swept at 100
mV-s\(^{-1}\), which is likely due to the relatively slow kinetics for bulk charge injection. Output curves for P3CPT-based OECTs also exhibit working operation at low gate voltages (\(|V_G| < 1\) V) with saturation at high drain currents, consistent with other OECT device characteristics in literature.

**Figure 27** – (a) Transfer curve for P3CPT films cast onto Micrux Pt-interdigitated electrodes (total area = 38.5 mm\(^2\), 90 pairs, 10 µm electrode length, 10 µm electrode gap, \(d = 140-190\) nm). The gate electrode is an Ag/AgCl wire, and the electrolyte is 0.1 M NaCl/H\(_2\)O. The drain voltage \(V_D\) is held at -0.6 V. The inset is a logarithmic plot of the drain current to demonstrate the on-off ratio. (b) Output curves, where the drain voltage \(V_D\) is varied from 0.0 to -0.6 V, and the gate voltage \(V_G\) is varied in 0.1 V increments from 0.0 V to -0.8 V. (c) Plot of transconductance corresponding to the transfer curve, with \(V_D = -0.6\) V.

A crucial parameter for estimating the signal amplification of the active material is the transconductance \(g_M = \Delta I_{DS}/\Delta V_{GS}\), which quantifies the incremental change in gate potential needed to induce a change in the source-drain current. OECT devices fabricated with P3CPT exhibit an average maximum transconductance of 26 ± 2 mS at \(V_{GS} \approx -600\) mV (Figure 27c), which is among the highest reported. The non-monotonic dependence of transconductance on gate voltage can be attributed to the influence of disorder on the electronic transport properties of P3CPT.\(^{51}\) It is also important to highlight that the hexyl
variant of the carboxylic acid-based polymer has been previously spincoated into p-channel interdigitated OECTs from dimethyl sulfoxide, with an average maximum transconductance of 12 mS at $V_{GS} \approx -600$ mV.49 While the maximum transconductance is achieved at similar gate biases between the two polymers, increases in transconductance in our material could be attributed to disparate processing conditions, as well as polarity differences stemming from use of a shorter alkyl spacer between the polymer backbone and the carboxylic acid group.

As a caveat, interdigitated OECTs exhibit higher effective $W/L$ ratios than planar OECTs for the same areal footprint. In planar OECTs, the transconductance is reported to be proportional to $Wd/L$, where $W$, $d$, and $L$ refer to the width, film thickness, and length of the channel respectively.27, 55, 83, 84 With high effective $W/L$ ratios, interdigitated OECTs tend to have higher transconductance than their planar counterparts. However, it has been reported that transconductance does not have a straightforward linear dependence on the $Wd/L$ ratio.85 Thus, quantifying any proposed materials-dependent parameter (e.g. $\mu C^*$) is difficult, and future device studies should be completed on both planar and interdigitated OECTs to more thoroughly understand device scaling metrics.

2.3.6 Conclusions

Herein, we report a carboxylated polythiophene as a conjugated polyelectrolyte-based OECT material that demonstrates fast redox kinetics, dual electroactivity in both aqueous and organic electrolytes, competitive pseudocapacitance, and facile aqueous processability. Films can be easily spray-cast from water without requiring dispersants or organic co-solvents, followed by a simple post-processing acidification step which renders
the material resistant to delamination and dissolution in common solvents. This allows for versatile redox activity and enables clear elucidation of structure-property relationships without the obfuscating effect of additives, which can compromise performance and compositional purity. The processability of the material is also desirable for many large-scale printed electronic applications, where the use of benign solvents is often desirable for mitigating the health, environmental, and financial consequences of halogenated aromatic solvents or other volatile organics. P3CPT is the first conjugated polyelectrolyte to be used as an active material in its pristine form for OECTs without the need for crosslinkers or ion exchange to produce stable, water-insoluble films. We also support the notion that the use of carboxylic acid substituted side chains can be used as tunable solubility modifiers; addition of alkyl carboxylic side chains can render polymer backbones insoluble in the protonated acid form, but the same materials can be rendered aqueous-processable as a deprotonated carboxylated salt. Notably, this is the first adaptation of this strategy toward OECT devices. Functionalization would be an excellent strategy to modify existing p- and n-channel backbones to yield highly competitive and processable OECT active materials.

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Khau, B.V.; Savagian, L.R.; De Keersmaecker, M.; Gonzalez, M.A., Reichmanis, E. Carboxylic Acid Functionalization Yields Solvent-Resistant Organic Electrochemical Transistors. ACS Mat. Lett., 2019, 1, 599-605. 86
CHAPTER 3. IMPACT OF ALKYL SPACER LENGTH ON ELECTROCHEMICAL DOPING OF CARBOXYLATED POLYTHIOPHENES

3.1 Introduction

Synthetic efforts to produce polymeric semiconductors with the ability to act as mixed conductors have employed the ad hoc strategy of appending the ion-conducting poly(ethylene oxide) side chain to the electron/hole conducting backbones used in the organic electronics field. This strategy has been used to great effect to produce aqueous-compatible polymers using thiophene, naphthalene-diimide, and other backbones, with dramatic effects on solvent intake and volumetric operation during doping. However, this strategy requires some restraint with respect to the side chain: making side chains increasingly hydrophilic (e.g. by increasing the length of ethylene oxide side chains) for the purpose of high swellability in aqueous media does not always yield higher performance. Above a critical threshold, increased hydration can severely disrupt electrical connectivity between polymer chains, decrease the effective charge-carrier mobility, and induce delamination at the polymer-electrode interface. An additional wrinkle not considered in these narratives is the significant decrease in glass transition that occurs when substituting alkyl for ethylene oxide side chains, in addition to increasing side chain length. Furthermore, the molecular weight average of these polymers frequently skews below 15-20 kg-mol⁻¹ and is hard to synthetically control when making a series of polymers for a given study.
Although side chain engineering is not as straightforward as depicted in academe, a significant knowledge gap exists for engineering of alternative side chains beyond the widely used ethylene oxide ones. We attempt to bridge this knowledge gap by expanding on the initial study of the carboxylated polythiophene in Chapter 2. Herein, the alkyl spacer length separating the polythiophene from the carboxylic acid end group is incrementally increased, as depicted below.

**Figure 28** – Carboxylated polythiophene series in this study. The alkyl spacers for these polymers have lengths 4 – 7 between the backbone and the acid end group.

This series of polymers is selected due to their clear similarities with the widely studied poly(3-alkylthiophene) P3AT series, in addition to our initial aqueous work with the P3C(Pr)T polymer (listed previously as P3CPT), which should enable indirect comparisons of our results to previous microstructural, electrochemical, and charge-carrier trends seen by increasing side chain length.

We hypothesize that cast films with longer side chains should exhibit enhanced interlayer structural ordering and increased interchain spacing, as observed in P3ATs, although the presence of the carboxylic acid terminated group may add additional steric interactions and inhibit directed self-assembly. Likely, carboxyalkyl functionalized
polymers demonstrate decreased crystallinity compared to their alkyl analogues, which may be attributed to intrachain crosslinking\textsuperscript{78, 91, 92}, as evidenced by previous x-ray diffraction studies.

Increases in side chain length should also intuitively decrease charge carrier transport, because a higher percentage of the polymer by mass is composed of insulating alkyl side chains. In the P3AT series, charge carrier mobility for films cast from chloroform showed decreases when moving from butyl to the decyl version of the polymer, although the increased processability and favorable microstructure of the hexyl polymer yielded it with the highest mobility. In this Aim, we determine whether interchain spacing as dictated by side chain/alkyl spacer length is a viable knob for which to tune both the microstructure of the polymer and its mixed conduction properties, especially in aqueous solution.

3.2 Experimental Methods

3.2.1 Materials

P3KButT (Poly(3-(Potassium-4-butanoate)thiophene-2,5-diyl), $M_w = 21$ kDa, PDI = 2.2, RR=89%), P3KPenT (Poly(3-(Potassium-4-pentanoate)thiophene-2,5-diyl), $M_w = 28$ kDa, PDI = 2.0, RR=89%), P3KHexT (Poly(3-(Potassium-4-hexanoate)thiophene-2,5-diyl), $M_w = 35$ kDa, PDI = 2.4, RR=86%), and P3KHeptT (Poly(3-(Potassium-4-heptanoate)thiophene-2,5-diyl), $M_w = 65$ kDa, PDI = 2.6, RR=85%) was purchased from Rieke Metals Inc. $\rho$-toluenesulfonic acid monohydrate ($\rho$TsOH-H$_2$O, 98%, Sigma-Aldrich), sodium chloride (99.9%, biotechnology grade, VWR), acetone, methanol, and isopropanol were used as received. Millipore-processed deionized (DI) water was used with a resistivity of 18.2 M$\Omega$-cm.
3.2.2 Film Preparation for Electrochemical and Transistor Measurements

Precursor solutions were dissolved in water at a concentration of 3 mg-mL⁻¹ and stirred at 50 °C to ensure complete dissolution. Notably, the longest side chain length polymer, P3KHeptT, did not dissolve in water, even after 90 days immersed in solution, likely due its large molecular weight. All other polymers were well-dissolved, where no particulates were observed after 48 hours prior to use.

ITO-coated glass slides (Delta Technologies, resistivity = 8–12 Ω sq⁻¹) were sonicated and cleaned via sonication in acetone, methanol, and IPA for 15 minutes each, followed by blow drying under a nitrogen air gun. To remove residual organic residues, the slides were irradiated with a UV-ozone cleaner (Novascan PSD-UV) for 30 minutes prior to precursor deposition.

The precursor polymer solutions were spray-cast (Iwata-Eclipse HP-BC Airbrush, 20 psi N₂) onto substrates heated to 80 °C to an average thickness of approximately ~150-300 nm. The spray-cast films were converted into their solvent-resistant acid form by immersing the films in 0.1 M para-toluenesulfonic acid monohydrate in methanol for 10 minutes, rinsing of the film in copious methanol to remove any excess pTsOH-H₂O, and subsequent drying under N₂ at 50 °C for 1 hr prior to any electrochemical and spectroscopic measurements.

3.2.3 Cyclic Voltammetry

Cyclic voltammetry was performed using a Gamry Reference 3000 Potentiostat/Galvanostat using a three-electrode setup. The working electrode consisted of
spray-cast films on ITO/glass electrodes, with the counter electrode being a Pt flag, flamed with a butane lighter prior to use. For aqueous testing, the reference electrode was a standard Ag/AgCl reference electrode (3M aqueous NaCl inner solution, BASi), with the electrolyte being 0.1 M NaCl in DI water. Argon was bubbled through the aqueous solution for 15 minutes prior to measurement. After degassing, argon was used to cover the top of the electrolyte solution to not disturb the system via convection. Scans were recorded with a step size of 2 mV.

3.2.4 Differential Pulse Voltammetry

Differential pulse voltammetry was performed using the same setup as in cyclic voltammetry. A 20 mV pulse was applied, with an integration time of 50 milliseconds and a step size of 1 mV.

3.2.5 Spectroelectrochemistry

The in situ spectroelectrochemical analyses were performed using an Agilent Cary 5000 spectrophotometer in quartz cuvettes (1 cm path length). The working electrode consisted of ITO-coated glass slides (Delta Technologies, resistivity = 8–12 Ω sq⁻¹) coated in the solvent-resistant form of the polymer, and a platinum flag was used as the counter electrode. An Ag/AgCl reference electrode (3M aqueous NaCl inner solution, BASi) was used to complete the three-electrode cell. The electrolyte consisted of a 0.1 M NaCl (99.9%, biotechnology grade, VWR) solution in Millipore water. Prior to recording spectra, the film was electrochemically conditioned by performing 10 cyclic voltammetric scans between -0.5 V and +0.9 V vs. Ag/AgCl with a scan rate of 50 mV s⁻¹ to ensure the film was quasi-equilibrated. After conditioning, the film was biased under potentiostatic
conditions in 100 mV steps, starting with the most cathodic potential and progressively biasing toward anodic conditions. Film spectra were recorded under potentiostatic conditions once the working electrode current had reached a steady-state (~30-60 seconds per 100 mV step).

3.3 Results and Discussion

3.3.1 Cyclic Voltammetry in Aqueous Solution

As a preliminary test, cyclic voltammetry was applied onto the spray-coated films of P3C(Pr)T, P3C(Bu)T, and P3C(Pe)T in 0.1 M NaCl(aq). (Figure 29, Figure 30, Figure 31). As an internal control, P3C(Pr)T was tested as well, as these experiments utilize a similar system, except with a Pt flag as the counter electrode instead of the stainless steel electrode used previously. At 50 mV-s⁻¹, the polymer series appear to show unipolar p-channel doping in this setup, as demonstrated by the formation of a broad oxidation onset > 0.2 V, although slight peaks in this regime can be covered by the monotonically increasing current density as the polymers are oxidized. The polymers were not oxidized past 0.5 V vs. Ag/AgCl to preclude degradation that could occur either through over-oxidation of the polymer or side reactions stemming from the breakdown of water. Additionally, there are slight differences in the polymers’ maximum current density, likely due to a combination of chemical affinities in aqueous solution and film thickness. However, such current densities are within less than half an order of magnitude of each other. Onsets of oxidation are also calculated for the polymer films with no clear trend with increased side chain length (P3C(Pr)T, -0.057 V; P3C(Bu)T, -0.298 V; P3C(Pe)T, -0.229 V).
Figure 29 – Cyclic voltammograms, 50 mV-s\(^{-1}\), of P3C(Pr)T in 0.1 M NaCl (aq).

Figure 30 – Cyclic voltammograms, 50 mV-s\(^{-1}\), of P3C(Bu)T in 0.1 M NaCl (aq).
3.3.2 Variation in Scan Rate – Reversibility and Doping Kinetics

In Aim 1, it was claimed that the voltammogram indicated a reversible voltammogram. This characterization is likely not true, especially after measuring how the lineshapes and approximate peaks change upon rapidly increasing the scan rate. A more suitable characterization is to describe these voltammograms as quasi-reversible. In this study, the peak corresponding to the reduction of the film in the reverse sweep is noted as a function of scan rate. When cycled up to 2000 mV-s⁻¹, the location of the peak shifts from > 0.4 V towards more reductive potentials, accompanied with an increasing lack of similarity between the anodic and cathodic sweep. (Figure 32, Figure 33, Figure 34) Qualitatively, P3C(Bu)T shows the largest left-shift in the reduction peak while P3C(Pe)T shows a more robust response, with smaller peak shifts and less impact of scan rate on line
shape. This difference suggests that the P3C(Pr)T polymer is less influenced by mass transport limitations at high scan rates than its two shorter side-chain analogues.

Figure 32 – Cyclic voltammograms of P3C(Pr)T taken at increasing scan rates from 10 – 2000 mV-s\(^{-1}\) in 0.1M NaCl.

Figure 33 – Cyclic voltammograms of P3C(Bu)T taken at increasing scan rates from 10 - 2000 mV-s\(^{-1}\) in 0.1 M NaCl (aq).
Figure 34 – Cyclic voltammograms of P3C(Pr)T taken at increasing scan rates from 10 - 2000 mV-s\(^{-1}\) in 0.1 M NaCl \((aq)\).

Plots of peak current density vs. scan rate were generated to approximate the critical scan rate where mass transport limitations started to dominate. From Figure 35, deviations from linearity towards a square-root dependence characteristic of mass transfer limitations are seen for all polymers close to 500 mV-s\(^{-1}\), which is what was observed in initial tests of P3C(Pr)T in Aim 1. To accurately pinpoint these regime transitions, log-log plots of current density vs. scan rate are generated. In this manner, expected power-law scalings are collapsed into linear trends, where the slope dictates the approximate power of the dependence. (Figure 36, Figure 37, Figure 38). Contrary to initial qualitative observations from examining the untransformed graph as in Aim 1, the linear regime only
occurs within a 1-2 order magnitude time window, with a superlinear regime emerging at extremely low scan rates.

**Figure 35** – Left: Plot of peak current as a function of scan rate for rates between 10-2000 mV-s⁻¹. Right: Zoomed-in plot of peak current vs scan rate for 10-500 mV-s⁻¹, to provide more visual clarity at low scan rates.

**Figure 36** – Log-log plots of current density vs. scan rate for P3C(Pr)T.
**Figure 37** – Log-log plots of current density vs. scan rate for P3C(Bu)T.

**Figure 38** – Log-log plots of current density vs. scan rate for P3C(Pe)T.
If the resistance between the polymer film and electrode is considered negligible, and the films are uniform and thin, then it can be assumed that these measurements approximate the kinetics of processes coupled with ion migration. These regimes are tabulated for each polymer (Table 3), where we note that further polymer systems should be tested to determine if a trend exists. As expected from the initial analysis on the polymer scan rates, the longest side chain polymer has the largest critical scan rate prior to mass transfer limitations, although no trend is concretely observed for this small family of polymers.

**Table 3** – Approximate regime cutoffs for the polymers tested in this study.

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<th>Polymer</th>
<th>Superlinear (diffusion-limited)</th>
<th>Linear (adsorption-limited)</th>
<th>Square-root (mass transfer limited)</th>
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<td>&lt; 50 mV·s⁻¹</td>
<td>50-500 mV·s⁻¹</td>
<td>&gt; 500 mV·s⁻¹</td>
</tr>
<tr>
<td>P3C(Bu)T</td>
<td>&lt; 50 mV·s⁻¹</td>
<td>50-300 mV·s⁻¹</td>
<td>&gt; 300 mV·s⁻¹</td>
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</tbody>
</table>

### 3.3.3 Aqueous Spectroelectrochemistry of solvent-resistant polymers

In addition to the electrochemical studies provided above, spectroelectrochemistry was used to monitor the evolution of charged and neutral states as a function of potential. In all such polymers, a decrease in features associated with neutral states in the 2-2.8 eV range (500-600 nm) is observed with a concomitant increase in a charged feature in the near-IR in all tested polythiophenes. The presence of an isobestic point also indicates that the polythiophene species undergo oxidative doping with no additional processes with different stoichiometry, at least in this voltage range. As cast, the polythiophenes appear to
demonstrate H-like aggregation\textsuperscript{93}, where the low-energy peak at 2.07-2.08 eV (likely related to the 0-0 transition) is smaller than the peak at 2.25-2.29 eV (likely related to the 0-1 transition). As these spectra are taken in the presence of a solvent with the examined polymer being electrochemically doped, the photophysical picture as described by Spano and Silva may not be applicable here.

**Figure 39** – Voltage-dependent spectra of P3C(Pr)T from -0.5 V (black) to 0.5 V (blue) vs Ag/AgCl in 0.1 M NaCl.

**Figure 40** – Voltage-dependent spectra of P3C(Bu)T from -0.5 V (black) to 0.5 V (blue) vs Ag/AgCl in 0.1 M NaCl.
Figure 41 – Voltage-dependent spectra of P3C(Pe)T from -0.5 V (black) to 0.5 V (blue) vs Ag/AgCl in 0.1 M NaCl.

3.3.4 Comparison of Apparent Oxidation Offsets

The combination of absorption and electrochemical characterization of these polymers enables direct comparisons between two different landscapes: (1) charging from a strictly electrochemical standpoint and (2) formation of charged features from a spectroscopic standpoint.

Charging from an electrochemical standpoint can be approximated by examining the oxidation onset of the steady-state voltammograms of these polymers and remeasured through differential pulse voltammetry (DPV) to eliminate the influence of background currents. (Figure 42, Figure 43, Figure 44) From a spectroscopic standpoint, the absorbance of neutral and charged features can be plotted as a function of potential to estimate the initial onset where the spectra begins to appreciably change.
Figure 42 – Oxidation onset as measured via differential pulse voltammetry for P3C(Pr)T. Only two films were measured due to accidental delamination of film 3.

Figure 43 – Oxidation onset as measured via differential pulse voltammetry for P3C(Bu)T.
Figure 44 – Oxidation onset as measured via differential pulse voltammetry for P3C(Pe)T.

For the approximations of absorption onset, the feature ascribed to the 0-1 transition and the charged feature are plotted. (Figure 45, Figure 46). Although the shortest-side chain polymer P3C(Pr)T has a higher oxidation onset than the other two polymers as measured via DPV, this trend of oxidation onset vs side chain length is not linear as is demonstrated by approximate onsets from spectroelectrochemistry (measured via the 0-1 feature, Figure 45). The threshold potential for overoxidation of the polymer film can also be noted by examining the decrease in absorbance of the charged feature. A comparison of these values is tabulated in Table 4.
Figure 45 – Absorbance vs potential for the 0-1 feature for P3C(Pr)T, P3C(Bu)T, and P3C(Pe)T. Colored lines depict the qualitative onset of oxidation.

Figure 46 – Absorbance vs potential for the charged feature for P3C(Pr)T, P3C(Bu)T, and P3C(Pe)T. Colored lines depict the onset of decomposition or overoxidation.
Table 4 – Oxidation onset of carboxylated polythiophenes in 0.1 M NaCl measured by three different methods.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Spectroelectrochemistry</th>
<th>CV</th>
<th>DPV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3C(Pr)T</td>
<td>0.2</td>
<td>-0.057</td>
<td>-0.115</td>
</tr>
<tr>
<td>P3C(Bu)T</td>
<td>0.1</td>
<td>-0.298</td>
<td>-0.172</td>
</tr>
<tr>
<td>P3C(Pe)T</td>
<td>0.0</td>
<td>-0.229</td>
<td>-0.149</td>
</tr>
</tbody>
</table>

From this table, the relative onset as predicted by electrochemical methods (CV, DPV) occurs at lower potentials than predicted by spectroelectrochemistry. In other words, charging and electrochemical doping begins to occur in this series of polythiophenes prior to significant changes in the spectral lineshapes.

3.4 Future Directions and Conclusions

3.4.1 Scan Rate Kinetics

In this work, incremental changes in side chain length do not yield significant changes in the electrochemical doping behavior of carboxylated polythiophenes. While the longest side chain polymer demonstrates linear charging behavior up to 1000 mV-s\(^{-1}\), in contrast to the other two polymers (500 and 300 mV-s\(^{-1}\)), the approximate timescale for turn-on in a 500 mV window range from 0.5 s for the best polymer to 1.6 s for the slowest polymer), which is not a significant improvement. Regardless, techniques such as electrical impedance spectroscopy (EIS) and device measurements in OECTs may provide pertinent information regarding the charge-storage and effective coupled transport of these polymers.

Charging from an optical and electrochemical standpoint was also observed in tandem to preliminarily examine the relation between polymer charging and spectral
evolution. Through CV, DPV, and spectroelectrochemistry, these polymers exhibit charging behavior prior to significant spectral changes. This result is contradictory to the narrative laid out by Bargigia et al., who observed the reverse in a p-doping poly(propylenedioxythiophene) (PProDOT) polymer functionalized with ethylene oxide side chains. In the PProDOT narrative, the authors point to the evolution of a subgap state prior to the formation of mobile charge carriers to explain significant spectral evolution observed prior to charging measured via electrochemical measurements.

A possible explanation that could contribute to the differences observed here is the utilization of hydrophobic sidechains with a polar end group, which will contribute to a less polar environment for electrochemical doping compared to the PProDOT polymer. Future experiments involving modulating the environmental polarity, either through experimentation in a polar aprotic solvent such as propylene carbonate, or utilization of more hydrophobic or hydrophilic side chains, would be useful additional work to reconcile the apparent contradiction noted here compared to Bargigia et al.
CHAPTER 4.  CARBOXYLIC ACID FUNCTIONALIZATION OF N-TYPE DIKETOPYRROLOPYRROLE POLYMERS

4.1  Introduction

As demonstrated in the previous two chapters, functionalization of polythiophenes with carboxylic acid side chains results in significant aqueous electroactivity not observed in the unmodified alkyl counterpart, poly(3-hexylthiophene). Consequently, it was hypothesized that functionalization of more advanced backbones beyond polythiophene may yield high-performance polymers.

4.1.1  Synthetic Design Rationale (in collaboration with Dr. Audrey Scholz, Chemistry)

We initially selected the donor-acceptor paradigm for this work, as alternating donor-acceptor moieties likely demonstrate backbones with higher charge-carrier mobility than their polythiophene counterparts. In theory, attractive interactions between adjacent units should provide a large charge transfer integral for efficient hopping kinetics, leading to improved charge transport.95

Diketopyrrolopyrrole (DPP) was used as the acceptor unit due to its tight pi-pi stacking and large coplanar structure, and has been used to great effect to produce polymers that yield transistors with charge carrier mobilities exceeding 10 cm² V⁻¹ s⁻¹. 96-99 Although these values may be overestimated due to inappropriate model fitting11, 100 and influenced by mobility hype in the literature, they are likely at least an order of magnitude higher than thiophene-based polymers.
While the previous “high mobility” polymers used thiophene-flanked DPP, thiazole flanking was employed here because (1) it yields a more coplanar structure (0 degree dihedral angle via DFT calculations) compared to the thiophene analogue, and (2) appears to have more stable charge transport, with previous thiazole-DPP – bithiazole polymers synthesized in our group demonstrating 0.2 eV higher ionization potential and electron affinities than thiophene-flanked DPP – bithiazole polymers.\textsuperscript{101, 102} The electron-rich bithiophene unit was used as the donor unit to provide moderate degrees of flexibility in the backbone to improve potential interactions with ions.

To make the polymer backbone soluble and introduce groups to facilitate ion transport, alkyl sidechains with methyl ester end groups were selected. These groups were chosen for ease of synthesis and potential solubility switching, as evidenced in Chapter 2. Specifically, the synthesized polymer with organic end groups was expected to be processible in organic solvents, and upon saponification and hydrolysis, can be made into water-soluble and solvent-resistant forms of the polymer. (\textbf{Figure 47}) This strategy was effectively used to process solvent-resistant materials from solvent-processible precursors from electrochemical studies. \textsuperscript{69, 86}
4.1.2 Expected Impact

This polymer is expected to operate as an n-channel semiconductor with aqueous electroactivity. To date, the number of polymeric semiconductors that are aqueous electroactive are small, with most candidates functioning as p-channel materials. This tendency can be attributed to the additional difficulty and care required to make materials designated for n-channel operation. Such materials are susceptible to oxidizing environments such as ambient air and water—often requiring vacuum or controlled environments to maintain stability in these polymers.

In the OFET field, air-stable polymers operating in N-channel operation are achieved by targeting LUMO levels of deeper than -4.0 eV, as indicated by Figure 48. It is important to note that this graph is based on LUMO levels calculated from small-molecule
semiconductors. While this rule of thumb may not necessarily apply to polymeric semiconductors, the selection of units has been designed with this energetic requirement in mind.

Figure 48 – Depiction of several small molecule organic semiconductors, demonstrating the relation between LUMO levels and ambient stability.103

4.2 Experimental Methods

Methods for synthesis, thermal characterization, OFET performance, and processing can be found in Dr. Audrey Scholz’s doctoral thesis. An abbreviated summary of the synthetic schemes for making the polymers for this chapter is pictured in Appendix B. The methods described here refer to electrochemical measurements that I have performed in this collaboration.
4.2.1 Materials

Polymers pOMeDPPTz-BTh and pK⁺DPPTz-BTh were used as received from Audrey Scholz. p-Toluene sulfonic acid monohydrate (pTsOH-H₂O, 98%, Sigma-Aldrich), sodium chloride (99.9%, biotechnology grade, VWR), 1,2,4-trichlorobenzene, acetone, methanol, and isopropanol, and propylene carbonate were used as received. Tetrabutylammonium hexafluorophosphate was recrystallized in hot ethanol prior to use. Millipore-processed deionized (DI) water was used with a resistivity of 18.2 MΩ-cm. Indium tin oxide (ITO)/glass (sheet resistance = 8-12 Ω-sq⁻¹, Delta Technologies) substrates were used as received.

4.2.2 Preparation of Working Electrodes for Electrochemical Measurements

Prior to film preparation, the methyl ester pOMeDPPTz-BTh was dissolved into 1,2,4-trichlorobenzene to a concentration of 10 mg-mL⁻¹ and stirred overnight on a hot plate at 105°C for complete polymer dissolution. Similarly, the water-soluble potassium salt pK⁺DPPTz-BTh was dissolved in DI water to a concentration of 3 mg-mL⁻¹ and stirred overnight on a hotplate at 50 °C to ensure complete polymer dissolution.

ITO substrates were cleaned via sonication in acetone, methanol, and isopropanol for ten minutes, followed by irradiation under a UV-ozone cleaner (Novascan PSD-UV) to remove residual organic residue. The water-soluble pK⁺DPPTz-BTh polymer solutions were spray-cast (Iwata-Eclipse HP-BC Airbrush, 20 psi N₂) onto ITO/glass substrates heated to 80 °C. The spray-cast films were converted into their solvent-resistant acid form by immersing them in 0.1 M para-toluene sulfonic acid monohydrate in methanol for 10 minutes, followed by rinsing of the film in copious methanol to remove any excess pTsOH-
H₂O, rinsing under water to remove unprotonated polymer residues, and subsequent drying under N₂ at 50 °C for 1 hr.

The methyl ester polymers could not be realistically spray-coated due to the high boiling point of 1,2,4-trichlorobenzene. Additionally, heated blade coating of the methyl ester polymers proved unsuccessful on ITO/glass substrates, although future attempts coupled with primer layers may prove successful. 1 µL of pOMeDPPTz-BTh solutions was dropcast onto glassy carbon button electrodes (BASi, 3mm diameter) and dried in an oven at 100 °C for 20 minutes.

4.2.3 UV-Visible Spectroscopy

To examine subtle changes stemming from acidification of the water-soluble precursor, UV-visible spectra (Agilent Cary 4000) were collected with the transparent ITO/glass substrates spray-coated before and after acidification. An ITO/glass slide undergoing the same cleaning treatment and UV-ozone irradiation was used as the blank.

4.2.4 Cyclic Voltammetry (CV)

Cyclic voltammetry was performed using a Gamry Reference 3000 Potentiostat/Galvanostat using a three-electrode setup. The working electrodes for the aqueous and organic solutions are spray-coated films on ITO slides and drop-cast films on button electrodes, respectively. The counter electrode comprised Pt flag flamed with a butane lighter prior to use. For aqueous testing, the reference electrode was a standard Ag/AgCl reference electrode (3M aqueous NaCl inner solution, BASi), with the electrolyte being 0.1 M NaCl in DI water. For organic testing, the reference electrode was an Ag/Ag⁺
electrode made in-house. This pseudoreference consisted of an Ag wire suspended in 0.5 M AgNO₃/acetonitrile and was calibrated as 85 mV vs the ferrocene/ferrocenium redox couple. The electrolyte in the organic solution was 0.1 M TBAPF₆ in propylene carbonate. All electrolytes were degassed with argon flow for 15 minutes prior to and during measurement. Scans were recorded at a scan rate of 50 mV s⁻¹, with a step size of 2 mV.

4.3 Results and Discussion

4.3.1 Initial protonation studies on water-processible polymer

Initial proof-of-concept acidification studies were completed starting with the water-processible polymer to determine whether the water-soluble polymer can be made into a solvent-resistant form. When the acidification procedure was applied to the spray-cast pK⁺DPPTz-BTh films, the resulting films are completely insoluble in water and do not dissolve even after immersion overnight. Thus, this polymer has likely been converted from the carboxylate to the carboxylic acid, but surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared spectroscopy (FTIR) are necessary to confirm this hypothesis.
During this process, (unnormalized) UV-visible spectra was collected before and after acidification to quantify any spectral differences. (Figure 50). No visible color changes or film quality differences were observed, other than the solubility switch attained as aforementioned. In terms of spectral changes, the acidified polymer demonstrates a lower absorption, indicating the protonated polymer either (1) has a lower absorption coefficient or (2) unprotonated polymer is removed during the acidification process, decreasing the effective polymer absorbance. J-like aggregation is also observed, evidenced by increased absorption of the lower-energy peak at ~770-780 nm relative to the higher-energy peak at ~700 nm. Additionally, a small red shift is also observed in the film of the acidified polymer and can be attributed to the formation of interchain interactions in polymers with latent hydrogen bonding. As a sanity check, this spectrum was also
compared to that of **PDBTz**, a previous polymer developed by the Reichmanis group, as **PDBTz** shares multiple similarities with the polymer in this study. (**Figure 51**)
Figure 52. (a) Solution spectra of PDBTz in various solvents. (b) Film spectra of PDBTz casted from various solvents. Figure from Fu et al.102

Notably, the spectra of the acidified polymers are close to those of PDBTz, even though the chemical structure of pCOOHDPPTz-BTh has “reversed” units (thiazole flanking instead of thiophene flanking, bithiophene instead of bithiazole). Audrey Scholz also collected spectral data on the methyl ester version of this polymer in solution and film, pOMeDPPTz-BTh, showing similar peak locations to the other functionalized analogues. (Appendix B, Figure 63).

4.3.2 Estimation of Frontier Orbital Levels

As the optical bandgap of the polymer with carboxylic acid functionality is roughly like that of the ester-functionalized polymer, we expect that the frontier orbitals measured via cyclic voltammetry should likewise be close. This observation can be reasoned by noting that the impact of side chains on the conjugated polymer backbone should be
limited, especially as the charged or ionizing group is far away from the backbone. Cycling the ester polymer dropcast on a glassy carbon electrode in 0.1 M TBAPF₆/propylene carbonate yields well-defined and reversible redox behavior. (Figure 53).

**Figure 53** – Cyclic voltammograms of pOMeDPPTz-BTh polymer in organic electrolyte. Films were dropcast on glassy carbon button electrodes and cycled at 50 mV-s⁻¹. A blank ITO slide was also cycled prior to measurement to determine the approximate electrochemical stability window.

The shape of the voltammogram is characteristic of donor-acceptor polymers with wide bandgaps, as evidenced by the >1 V separation between the oxidation and reduction peaks. To estimate the frontier orbital energies from the cyclic voltammogram, the steady-state peaks corresponding to the oxidation and reduction onset are located at -1.43 V (vs. Fc/Fc⁺) and 0.73 V (vs. Fc/Fc⁺). The ferrocene/ferrocenium couple can be used to mathematically relate the electrochemical potential to the frontier level orbital energies in
a band diagram. This relation is achieved by noting that another reference electrode, the standard calomel electrode (SCE) is 4.7 eV vs vacuum\textsuperscript{105}, and Fc/Fc\textsuperscript{+} is 0.380 V vs. SCE\textsuperscript{76}, so the formal electrochemical potential of Fc/Fc\textsuperscript{+} is approximately -5.1 eV\textsuperscript{106,107} Thus, the approximate energies for the HOMO and LUMO of pOMEDPPTz-BTh, estimated as ionization potential and electron affinity, are 5.83 eV and 3.86 eV vs vacuum, respectively.

4.3.3 Electroactivity of ester and carboxylic acid polymers in aqueous solution

We hypothesized that the aqueous response of the ester and carboxylic acid polymers would follow the organic response of the ester, especially as the carboxylic-acid functionalized polythiophene in Chapter 2 demonstrated voltammograms with distinctly similar characteristics, such as a lack of a reduction onset and broad oxidation behavior (Figure 18) when cycled in both aqueous and organic electrolytes.

Upon cycling both pOMeDPPTz-BTh and pCOOHDPPTz-BTh in aqueous solution, it is immediately apparent that such polymers demonstrate poor electroactivity in aqueous solution, with some distinct differences between the two. The ester polymer demonstrates stable cycling in aqueous solution with broad features, in contrast to the cycling seen in organic solution. Additionally, the maximum current density of the ester polymer is only 5-10 times larger in magnitude compared to the control. The carboxylic acid polymer exhibits obvious signs of incompatibility in aqueous solution. pCOOHDPPTz-BTh immediately decays in maximum current density by >30% per cycle, indicating degradation. This hypothesis is also corroborated by the consistent lack of reversibility seen in the far edges of the polymer (E < -0.6V and E>0.4 V), as well as the disappearance of an oxidation peak at E = 0.35 V after the first cycle. (Figure 56)
Figure 54 – Cyclic voltammograms of pOMeDPPTz-BTh in 0.1 M NaCl (aq). Films were dropcast from 1,2,4-trichlorobenzene onto a glassy carbon electrode and cycled at 50 mV-s$^{-1}$. 

![Cyclic voltammograms](image)
Figure 55 – Overlaid voltammogram of 10\textsuperscript{th} cycle of pOMeDPPTz-BTh’s response with control.

Figure 56 – Cyclic voltammograms of pCOOHDPPTz-BTh in 0.1 M NaCl (\textit{aq}). Films were spraycast from aqueous solution onto ITO/glass substrates and cycled at 50 mV-s\textsuperscript{-1}.
4.4 **Future Directions and Conclusions**

Contrary to initial expectations, the poor aqueous electroactivity and stability of these polymers deems them incompatible for further testing in electrochemical transistors.

We speculate that the donor-acceptor backbone, with an approximated LUMO level shallower than -4 eV, was energetically not stable enough for stable water operation. We initially reasoned that the long alkyl spacers of length 13 made the polymer too hydrophobic for aqueous operation, but previous work by Audrey indicates that the ester form of the polymer is somewhat hydrophilic, with excellent coatings on untreated glass substrates over substrates treated with surface monolayers for OFET operation.

Additionally, upon saponification of the ester, the resulting potassium carboxylate $pK^+$DPPTz-BTh exhibited moderate solubility in water, forming a dispersion. This also indicates that even when the side chain end groups are converted to ionizing groups, the polymer is not charged enough to fully solubilize in aqueous solution, in contrast to the carboxylated polythiophenes from Chapters 2 and 3. Because the end groups along the side chain are so far removed from the backbone, the polymer likely behaves like one with purely alkyl side chains and would demonstrate notable charge-carrier mobilities in an OFET configuration instead.
5.1 Conclusion

The main directive of this thesis was to explore the potential applicability of carboxyalkyl side chains in endowing aqueous electroactivity to several conjugated polymer systems. The capability of these systems for aqueous electroactivity was gauged by primarily examining their electrochemical behavior as thin films; critical techniques such as cyclic voltammetry and spectroelectrochemistry enabled direct observation of the polymers’ charging behavior and spectral changes during redox changes.

In Aim 2, a proof-of-concept case for ionically-facilitating polymers was established for poly[3-(4-carboxypropyl)thiophene] (P3C(Pr)T). This initial exploration was inspired by works from Krysten Minnici and Yo Han Kwon in the tangential area of batteries, where they discovered that incorporation of the potassium carboxylate version of P3C(Pr)T as a binder resulted in improved charge capability after 200 cycles over state-of-the-art materials such as polyvinylidene fluoride. Inspired by this work, P3C(Pr)T as the acidified version of this water-soluble polymer was investigated for its potential use as an aqueous-electroactive conjugated polymer system. Notably, P3C(Pr)T demonstrates charging up to 500 mV-s\(^{-1}\) prior to mass transport limitations, yielding an estimated on/off speed of ~ 1 second and volumetric pseudocapacitance of 150 F-cm\(^{-3}\), comparable or better than other conjugated polyelectrolyte systems explored in literature.

In Aim 3, the effect of side chain length was investigated on the doping kinetics and spectral evolution of the polymers. Alkyl spacers were chosen between 3-6, for future
comparisons to alkylthiophene analogues such as P3HT. Although there were clear
differences in doping kinetics, with linear kinetic limits varying between 300, 500 and 1000
mV-s\(^{-1}\), no clear relationships were established regarding the transport phenomena in these
polymers from an electrochemical standpoint. An interesting wrinkle that warrants further
investigation is noted upon comparison of the oxidation onsets; charging occurs prior to
substantial spectra evolution, which contrasts with the trends exhibited in P(ProDOT)
polymers, another p-channel polythiophene system.

In Aim 4, the potential applicability of carboxylic acid side chains for mixed
conductivity is applied to a donor-acceptor polymer comprising thiazole-flanked
diketopyrrolopyrrole and bithiophene units. This backbone was selected to provide a higher
potential charge-carrier mobility than the previously tested polythiophenes. Due to the
large bulkiness of the backbone, longer alkyl spacers of length 13 were chosen to solubilize
the polymer. Upon cycling in aqueous solution, current densities were less than an order
of magnitude larger than the blank control, indicating a lack of aqueous electroactivity. It
is possible that this side chain engineering strategy may not apply to differing backbones,
but this conclusion is nebulous because the polymer’s ambient stability may be limited by
its shallow LUMO level as opposed to incompatible side chain engineering. While this
polymer did not electrochemically dope to an appreciable amount in aqueous media, it
served as a competitive OFET in work completed by Audrey Scholz, with moderate
mobilities of up to 0.01 cm\(^2\)V\(^{-1}\)s\(^{-1}\).

5.2 Suggestions for Future Work

5.2.1 Examination of Local Order during Electrochemical Doping
A major project limitation faced when completing the work of Aim 2 was the lack of associated microstructural characterization. These include techniques for probing a variety of varying length scales, such as Raman and IR spectroscopy, grazing incidence X-ray scattering (GIWAXS). *In situ* or *in operando* techniques to monitor changes in polymer microstructure during electrochemical doping would provide insight in determining: (1) if/how does repeated cycling impact the steady-state microstructure of the polymer; (2) the spatial location of ions from electrolyte relative to the backbone and side chains, and how this varies with side chain chemical affinity; (3) differences in microstructure associated with the two onsets of charging as measured via spectroelectrochemistry or cyclic voltammetry.

A successful proposal at the Stanford Synchrotron Light Source (SSRL) involving X-ray scattering with *in situ* capabilities was planned for the 2020-2021 cycle but delayed due to the COVID-19 pandemic. In conjunction with beamline scientist Christopher Takacs, we intended to use a conical cell made from polyether ether ketone (PEEK), where electrolyte and a reference electrode were held at the top of the cell and pressed firmly against a working electrode comprising a thin film coated on Au. This setup was previously used to examine time-resolved dynamics related to acid-crystallized PEDOT:PSS.108
Figure 58 – Schematic depicting conical cell to be used for X-ray scattering measurements in situ.

Figure 59 – (Left) Conical cell close-up. The electrolyte is filled at the top and pressed firmly against a substrate inserted between the cone bottom and the self-aligning glass substrate. (Right) Electrochemical testing setup of a film in-house to verify electrochemical measurements were equivalent to those done in a standard two-electrode cell geometry.

Prior to scheduled in operando testing, a subset of ex situ measurements for P3C(Pr)T were completed at beamline 11-3 of SSRL with the assistance of Chris Takacs.
The purpose of these experiments were to qualitatively examine the microstructural impact of different casting methods and determine if such processing methods should be probed in future *in situ* experiments.

**Figure 60** – Cartesian and chi-plots of the GIWAXS spectra for P3C(Pr)T cast in three different ways. To capture the lamellar peaks for future integration (out-of-plane), the chi-plot was integrated between $\chi = 20-30^\circ$ and $q = 1.5-20$ nm$^{-1}$. The in-plane peaks relevant to pi-pi stacking were captured by integrating the chi-plot between $\chi = 70-80^\circ$ and $q = 1.5-20$ nm$^{-1}$.

The films appear to be somewhat isotropic with edge-on texture, with lamellar and pi-pi stacking behavior similar to the alkyl analogue poly(3-butylthiophene). There are
minor differences between the different casting methods. Notably, the intensity of the isotropic ring at $q \sim 17$ nm$^{-1}$ is quite large but has significant variance relative to the intensity of the lamellar peaks for different casting methods. Both the dropcasted and spraycasted polymer films have large isotropic intensities relative to the second lamellar peak at $q \sim 9.8$ nm$^{-1}$, but comparable intensities for the bladecast sample, suggestive of improved alignment for the blade coated sample. Little variance is observed in the shapes for in-plane peaks, which indicates the pi-pi stacking of polymers within the films is similar. Intensity variations can be attributed to deviations in thickness; the dropcast film was the thickest, followed by the spraycast and bladecast films. These preliminary experiments suggest that future microstructural experiments involving this polymer can be completed by using a single casting method. However, this observation does not rule out the possibility of differences when the films are electrochemically doped, and only applies to dry, as-cast films.

5.2.2 Blending of Carboxylated Polythiophenes with Poly(ethylene oxide)

An additional direction worth pursuing is the blending of the carboxylated polythiophene series with a variety of different polymers. Because conjugated polymers are weakly bound solids, minor changes in conformation and backbone order through processing, synthetic modifications, or blending can have a substantial impact on the resulting optoelectronic properties. The previous ex situ GIWAXS study indicates that processing potentially plays a minor role in dictating the as-cast microstructure of the polymer.
Compared to synthetic modification, blending is an experimentally accessible approach that has been used to great effect to modify the optoelectronic properties of conjugated polymers. For example, polymers such as P3HT have been used as components in semiconductor/insulator blends to favorably modify the semiconductor crystallinity and connectivity, yielding marked improvements in field-effect charge carrier mobility.\textsuperscript{109} An additional advantage of blending is to grant improved mechanical properties not achieved in conjugated polymers. P3HT is a mechanically brittle semiconductor, with low degrees of elongation before break\textsuperscript{110}; blending with a ductile polymer such as polystyrene or high-density polyethylene can make the resulting film more “plastic”, improving the degree of elongation prior to break and enabling conformal coatings that do not fracture upon bending.

Poly(ethylene oxide) (PEO) has also been used to blend with P3HT, resulting in significant red shifts in the spectra and an enhanced 0-0 to 0-1 ratio in both absorption and emission,\textsuperscript{111} suggested as changes in the torsional backbone order. In the context of aqueous electroactive polymers, blending with PEO is particularly attractive because PEO serves as a viable ionically conductive material for polymer electrolytes in batteries. Additionally, as these polymers are microstructurally similar to the poly(3-alkylthiophene) family, a compelling proof-of-concept experiment to try is to blend the carboxylated polythiophene in Aim 1 with PEO. By examining any changes in the absorption spectra, the impact of blending on torsional order can be explored.

10 mg-mL\textsuperscript{-1} solutions of PEO with a molecular weight of 250,000 kg-mol\textsuperscript{-1} and the water-soluble precursor P3K(Bu)T were blended together in discrete volume ratios of 0\%, 25\%, 50\%, and 75\% PEO. The solutions were heated overnight at 80 °C, and subsequently
bladecast from water on a heated stage (70 °C surface temperature). The optical images demonstrate changes in film color from a reddish purple to an orange, suggesting the presence of isolated polythiophene chains. (Figure 61) When probed with UV-Vis, the films with PEO (Figure 62) demonstrate the emergence of a new peak at 3.02 eV (411 nm), which is suggestive of isolated chains as seen in dilute solutions of polythiophenes. However, there are no shifts or enhancements of the 0-0 to 0-1 ratio upon addition of PEO using this method, indicating that PEO may have a weak impact on modifying the torsional order of the carboxylated polythiophene.

Figure 61 – Pictures of bladecast films of blends of the water-soluble precursor P3K(Bu)T with poly(ethylene oxide) (PEO), cast from water with a total polymer concentration of 10 mg-mL⁻¹.

Figure 62 – UV-visible spectra of P3K(Bu)T blended with PEO, coated on glass substrates.
APPENDIX A. FITTED EIS VALUES FOR CHAPTER 2.

The symbols for the following tabulated data can be found in the “Lists of Symbols and Abbreviations” section.

Table 5. P3CPT Film 1 (Cast area = 1.4 cm², thickness = 193 ± 15 nm)

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<td>32.0</td>
<td>1340</td>
<td>69.9</td>
<td>0.17</td>
<td>5.95E-3</td>
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<td>51.5</td>
<td>10.3</td>
<td>0.54</td>
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<td>2120</td>
<td>110</td>
<td>0.19</td>
<td>4.69E-3</td>
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<td>88.8</td>
<td>1.04</td>
<td>4.15E-3</td>
</tr>
</tbody>
</table>
Table 6. P3CPT Film 2 (Cast area = 1.4 cm², thickness = 140 ± 14 nm)

<table>
<thead>
<tr>
<th>$E_{cell}$ (V)</th>
<th>$R_e$ (Ω-cm²)</th>
<th>$C_{A,DL}$ (µF-cm²)</th>
<th>$C_{V,DL}$ (F-cm³)</th>
<th>$R_{CT}$ (Ω-cm²)</th>
<th>$C_A^*$ (µF-cm²)</th>
<th>$C^*$ (F-cm³)</th>
<th>$\tau_D$ (s)</th>
<th>$\chi^2$</th>
</tr>
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<tbody>
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<td>1010</td>
<td>71.9</td>
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<td>19.8</td>
<td>1.41</td>
<td>22.5</td>
<td>1710</td>
<td>121</td>
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</tr>
<tr>
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<td>26.2</td>
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<td>26.6</td>
<td>2100</td>
<td>149</td>
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Table 7. P3CPT Film 3 (Cast area = 1.4 cm², thickness = 177 ± 20 nm)

<table>
<thead>
<tr>
<th>$E_{\text{cell}}$</th>
<th>$R_e$</th>
<th>$C_{A,DL}$</th>
<th>$C_{V,DL}$</th>
<th>$R_{CT}$</th>
<th>$C_{*A}$</th>
<th>$C_{*}$</th>
<th>$\tau_0$</th>
<th>$\chi^2$</th>
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<tbody>
<tr>
<td>(V)</td>
<td>(Ω·cm⁻²)</td>
<td>(µF·cm⁻²)</td>
<td>(F·cm⁻³)</td>
<td>(Ω·cm⁻²)</td>
<td>(µF·cm⁻²)</td>
<td>(F·cm⁻³)</td>
<td>(s)</td>
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</table>
Figure 63 – UV-vis spectrum for pOMeDPPTz-BTh both in solution ($1 \times 10^{-6}$ M in 1,2,4-trichlorobenzene) and thin film state, collected by Audrey Scholz.
APPENDIX B. SYNTHESIS OF N-CHANNEL DPP POLYMERS

The following summary and schemes are courtesy of Dr. Audrey Scholz. Further information regarding synthetic schemes of intermediates, monomers, routine characterization (GPC), film processing, and OFET performance can be found in her doctoral thesis.

**Scheme 1.** Schematic representation of the synthetic procedure for monomer synthesis and subsequent polymerization to yield pOMeDPPTz-BTh.

**Scheme 2.** Schematic representation of the post-polymerization potassium salt side chain modification to yield pK⁺DPPTz-BTh.
Scheme 3. Schematic representation of the post-polymerization side chain acidification to yield the solvent resistant pCOOH-DPPTz-BTh.
REFERENCES


