ESTABLISHING DESIGN PRINCIPLES FOR POLYTHIOPHENES USED IN ELECTROCHEMICAL APPLICATIONS

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The Academic Faculty

by

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ESTABLISHING DESIGN PRINCIPLES FOR POLYTHIOPHENES
USED IN ELECTROCHEMICAL APPLICATIONS

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show the approximated baseline and offset tangents. The two oxidation onsets, given as the intersection of these two fits, onsets are labeled. Panels A-D have been adapted with permission with permission from the literature.© 2020 American Chemical Society.

**Supporting Figure 4.4.2**
- A) Scan rate dependent CV data for drop-cast films of p(g6T2-T) in 0.1 M NaCl/H2O. Each curve represents the tenth cycle out of ten scans performed at each scan rate.
- B) Normalized data from (A) for comparison.

**Supporting Figure 4.4.3**
- Charge retention for p(g3T2-T) films drop-cast on a glassy carbon button electrode and cycled repeatedly between -0.5 and +0.8 V vs. Ag/AgCl in degassed 0.1 M NaCl/H2O under an inert argon blanket.

**Supporting Figure 4.4.4**
- A) Two-dimensional representative GIWAXS pattern for p(g2T2-T) spray-coated in Si. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale.
- B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled.

**Supporting Figure 4.4.5**
- A) Two-dimensional representative GIWAXS pattern for p(g3T2-T) blade-coated in Si. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale.
- B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled. This figure has been adapted with permission with permission from the literature.© 2020 American Chemical Society.

**Supporting Figure 4.4.6**
- A) Two-dimensional representative GIWAXS pattern for p(g4T2-T) blade-coated in Si. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale.
- B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled. This figure has been adapted with permission with permission from the literature.© 2020 American Chemical Society.

**Supporting Figure 4.4.7**
- A) Two-dimensional representative GIWAXS pattern for p(g6T2-T) blade-coated in Si. Scattering intensities are represented linearly, following a purple-red color scale.
- B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled. This figure has been adapted with permission with permission from the literature.© 2020 American Chemical Society.
from the literature.© 2020, American Chemical Society.

Supporting Figure 4.4.8

- A) Two-dimensional GIWAXS pattern for p(g2T2) blade-coated in Si. Scattering intensities are represented linearly, following a purple-red color scale. B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled.

Figure 5.2.1

- Repeat unit structures of polar ProDOT copolymers, showing A) 2,2-dimethyl-ProDOT (DMP) based backbone, and B) various polar side chains with corresponding polymer names.

Figure 5.2.2

- Schematic showing blade coating of polymer BOE-DMP and thin film saponification process to access polymer OH-DMP.

Figure 5.2.3

- CV traces of A) BOE-DMP and OH-DMP films, and B) polar PProDOT films recorded at 50 mV s⁻¹ in degassed 0.1 M NaCl/H₂O. Films (initial deposited polymer mass = 16 μg) were drop-cast from solution on GC button electrodes. Current is normalized to electrode area (a = 0.07 cm²).

Figure 5.2.4

- Average potential-dependent volumetric capacitance (C*) for polar PProDOT films measured in a degassed electrolyte of 0.1 M NaCl/H₂O. Capacitance was determined by EIS and normalized to the volume of the dry de-doped film. Error bars represent standard deviation of C* measurements performed on 3+ different films, cast and measured separately.

Figure 5.2.5

- Superimposed CV traces of G3-DMP performed on spray-cast films on ITO/glass in 0.5 M NaCl/H₂O from cycle 1 (black) to 1000 (light blue). The cumulative charge passed is shown as a function of number of redox cycles.

Figure 5.2.6

- Superimposed UV-Vis-NIR absorption spectra of polar PProDOTs biased at -0.8 V vs. Ag/AgCl in 0.1 M NaCl/H₂O, labeling 0-0 and 0-1 transitions.

Figure 5.2.7

- Potential-dependent UV-Vis-NIR absorption spectra of polar PProDOT films A) OH-DMP, B) G2-DMP, C) G3-DMP, D) G4-DMP. Films cast on ITO/glass and biased in 0.1 M NaCl/H₂O. Potentials are reported vs. Ag/AgCl.
Figure 5.2.8 – Representative GIWAXS patterns for polar PProDOTs films. Casting method is indicated in white text: A) OH-DMP, with detector artifact shown as a red line, B) G2-DMP, C) G3-DMP, and D) G4-DMP. For panels B-D, intensities are normalized to film thickness as measured by a profilometer. Scattering intensities are represented linearly on a purple-red color scale. Not that the absolute scattering intensity for panel A cannot be compared to B-D, as this sample was analyzed at a different beamline.

Figure 5.2.9 – Planar OECT characteristics for a device fabricated with G3-DMP. A) Transfer curve with corresponding transconductance (gm) $V_D = -0.5$ V. B) Output curves for gate voltages ranging from +0.10 V to -0.80 V recorded every 0.05 V. Data correspond to a sweep rate of 0.20 V s$^{-1}$ and device with channel dimensions of 50 μm × 50 μm (W×L), a film thickness $d = 282$ nm, and an ambient electrolyte of 0.1 M NaCl in H2O in ambient conditions. Arrows indicate the direction of the sweep. Figure has been adapted with permission from the literature.© 2018 Wiley-VCH.

Figure 5.2.10 – Plot of volumetric capacitance $C^*$ vs. mobility $\mu$ for p-type or ambipolar OECT materials as tested in pOECTs under similar conditions. The $C^*$ and $\mu$ of G3-DMP (purple star) is shown relative to the state-of-the-art p-type materials, including glycolated polythiophenes/polythienothiophenes (PT/PTT, yellow triangles), PEDOT-based systems (PEDOT, blue circles), a glycolated BTD derivative (BDT, green diamond), and a thiophene-based polyelectrolyte (PTHs, magenta square). All literature values for $\mu$ and $C^*$ for these reference materials were adapted from Inal et al.© 2018 Wiley-VCH.

Figure 5.2.11 – Thickness-normalized peak transconductance values for iOECT devices fabricated with PProDOTs operating in 1× PBS with a standard 3-terminal configuration. Error bars represent standard deviation of 3+ device measurements with active layers of different film thicknesses.

Figure 5.2.12 – A) Peak gm in iOECTs made with G3-DMP for varying channel thicknesses (d). Error bars for gm represent standard deviation of 3 different devices and 3 thickness measurements. B) Schematic of IDE set-up adapted from the Khan et al.© 2015, MDPI. The
A diagram depicts a bird’s eye view (left) and cross-sectional view (right) of an interdigitated platform used to study transport in a polymer film, showing electric field lines.

Supporting Figure 5.4.1 – Average water contact angle of DMP copolymers blade coated on glass. Error bars represent the standard deviation of three measurements.

Supporting Figure 5.4.2 – AFM height (left) and phase (right) images for A) BOE-DMP and B) OH-DMP blade coated on Si wafers. Imaging was done on dry films in standard tapping-mode (~150 kHz). $R_q$ represents the root-mean-square roughness averaged from three different 500 nm x 500 nm square areas on the film.

Supporting Figure 5.4.3 – Average water contact angle of DMP copolymers blade coated on glass. Error bars represent the standard deviation of three measurements.

Supporting Figure 5.4.4 – Absorption spectra of pristine BOE-DMP film (black), dry OH-DMP film after hydrolysis/rinsing (red), and OH-DMP film after electrochemical conditioning while holding at -0.4 V vs. Ag/AgCl in 0.1 M NaCl/H$_2$O (blue).

Supporting Figure 5.4.5 – Potential-dependent $C^*$ of blade-coated films of BOE-DMP and OH-DMP in degassed 0.1 NaCl/H$_2$O. $C^*$ was extracted from EIS and normalized to the volume of the dry de-doped film. Error bars for OH-DMP represent the standard deviation of 3+ films, cast and measured separately.

Supporting Figure 5.4.6 – Differential pulse voltammograms of thin films of polar PProDOTs: A) G2-DMP, B) G3-DMP, C) G4-DMP, D) OH$_2$-DMP and E) BOE-DMP, labeling the oxidation onsets. Polymer films were drop-cast on a GC button electrode and studied in a degassed 0.1 M NaCl/H$_2$O electrolyte under an argon blanket. Solid lines indicate data. Dashed lines indicate tangents for onset extraction.

Supporting Figure 5.4.7 – Scan rate dependence of CV peak current density for the aqueous-compatible polar ProDOT polymers: A) G2-DMP, B) G3-DMP, C) G4-DMP, and D) OH-DMP. Points connected with solid lines represent experimental peak current density. Dashed line represents the linear projection of peak current density, as determined by data...
recorded within non-diffusion limited scan rate regimes (v ≤ 50 mV s⁻¹) and fit to a linear regression.

**Supporting Figure 5.4.8** – Comparison of G3-DMP (shown here as “ProDOT(G3)-DMP”) and p(g3T2-T) from CHAPTER 4, showing A) percent charge retention over 1,000 doping/de-doping cycles in 0.1 M NaCl/H₂O for drop-cast p(g3T2-T) and 0.5 M NaCl for spray-cast G3-DMP. Identical voltage windows were used in the long-term cycling. B) CV traces of films (16 μg total mass) drop-cast on GC button electrode.

**Supporting Figure 5.4.9** – Potential-dependent absorption spectra of A) polymer BOE-DMP and B) polymer OH-DMP blade-coated on ITO/glass and biased in 0.1 M NaCl/H₂O.

**Supporting Figure 5.4.10** – Absorption spectra of blade- and spray-coated films of de-doped G3-DMP (“G3”) on ITO/glass while biased in 0.1 M NaCl/H₂O. Spectra are recorded after electrochemical conditioning under potentiostatic conditions. Potentials are reported vs. Ag/AgCl.

**Supporting Figure 5.4.11** – Normalized UV-Vis absorption spectra of films cast onto ITO/glass, including pristine/as-cast BOE-DMP, conditioned/de-doped BOE-DMP in an organic electrolyte (-0.8 V vs. Ag/Ag⁺ in 0.5 M TBAPF₆), and condition/de-doped OH-DMP in an aqueous electrolyte (-0.8 V vs. Ag/AgCl in 0.1 M NaCl/H₂O).– Normalized UV-Vis absorption spectra of films cast onto ITO/glass, including pristine/as-cast BOE-DMP, conditioned/de-doped BOE-DMP in an organic electrolyte (-0.8 V vs. Ag/Ag⁺ in 0.5 M TBAPF₆), and condition/de-doped OH-DMP in an aqueous electrolyte (-0.8 V vs. Ag/AgCl in 0.1 M NaCl/H₂O).

**Supporting Figure 5.4.12** – UV-Vis-NIR absorption spectra of films of two different batches of G3-DMP held at -0.8 V vs. Ag/AgCl in 0.1 M NaCl. The batches, which were synthesized by different individuals, were found to have a different GPC-determined molecular weights (in CHCl₃ at 40 °C vs. PS). Purple line: G3-DMP-JFP-22k, Mₙ = 22 kDa, Đ = 2.0. Red line: G3-DMP-BTD-41k, Mₙ = 41 kDa, Đ = 2.5.

**Supporting Figure 5.4.13** – Potential-dependent in situ conductance (black circles) and linear optical absorbance (red squares) at 1.31 eV (935 nm), corresponding to the polaron state, for spray-cast films of G3-DMP. Measurements were performed on
electrochemically doped films in ambient 0.5 M NaCl/H₂O.

Supporting Figure 5.4.14 – Two-dimensional representative GIWAXS pattern for G3-DMP films cast by A) blade-coating from chloroform and B) spray-coating from chloroform. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale.

Supporting Figure 5.4.15 – Two-dimensional representative GIWAXS pattern for G2-DMP films cast by A) spray-coating and B) spin-coating from chloroform. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale.

Supporting Figure 5.4.16 – Two-dimensional representative GIWAXS patterns of A) pristine blade-coated BOE-DMP, and B) OH-DMP, accessed through hydrolysis of blade-coated BOE-DMP. Scattering intensities represented linearly, following a purple-red color scale. Note that absolute scattering intensities cannot be compared, as the data were collected at different beamlines. Red line in panel B is an artifact of the detected and ought to be ignored.

Supporting Figure 5.4.17 – Representative iOECT characteristics for devices fabricated with G2-DMP, showing A) Transfer characteristics and corresponding transconductance, V_D = -0.60 V, B) Transfer curve on logarithmic scale superimposed on drain current. C) Output curves. Arrows indicate direction of the sweep.

Supporting Figure 5.4.18 – Representative iOECT characteristics for devices fabricated with G3-DMP, showing A) Transfer characteristics and corresponding transconductance, V_D = -0.60 V, B) Transfer curve on logarithmic scale superimposed on drain current. C) Output curves. Arrows indicate direction of the sweep.

Supporting Figure 5.4.19 – Representative iOECT characteristics for devices fabricated with G4-DMP, showing A) Transfer characteristics and corresponding transconductance, V_D = -0.60 V, B) Transfer curve on logarithmic scale
superimposed on drain current. C) Output curves. Arrows indicate direction of the sweep.—Representative iOECT characteristics for devices fabricated with G4-DMP, showing A) Transfer characteristics and corresponding transconductance, \( V_D = -0.60 \, \text{V} \), B) Transfer curve on logarithmic scale superimposed on drain current. C) Output curves. Arrows indicate direction of the sweep.

Supporting Figure 5.4.20 — Potential-dependent in situ conductance (black squares/lines) and transfer curve from a four-electrode OECT-like measurement (purple line, \( V_D = 0.4 \, \text{V} \), \( v = 50 \, \text{mV s}^{-1} \)) for G3-DMP films coated on interdigitated electrodes and studied under ambient conditions in a NaCl/H\(_2\)O electrolyte solution.

Figure 6.1.1 — Repeat unit structures of two polar-functionalized PProDOT copolymers, G3-DEHP and G3-DMP, which differ in the substitution of the aliphatic comonomer.

Figure 6.2.1 — A) CV of drop-cast films of G3-DEHP and G3-DMP 0.5 M NaCl/H\(_2\)O (\( v = 50 \, \text{mV s}^{-1} \)). B) Scan rate dependence of CV peak current density for both polymers 0.5 M NaCl/H\(_2\)O. Points connected with solid lines represent experimental peak current density. Dashed line represents the linear projection of peak current density.

Figure 6.2.2 — Normalized UV-Vis absorption spectra of neutral PProDOT films after electrochemical conditioning. Spectra were recorded while applying de-doping potentials (0.0 V for G3-DEHP and -0.4 V for G3-DMP) in 0.5 M NaCl/H\(_2\)O.

Figure 6.2.3 — Potential-dependent UV-Vis-NIR absorption spectra of G3-DEHP (A) and G3-DMP (B) cast onto ITO/glass and biased in 0.5 M aqueous NaCl/H\(_2\)O. Spectra are reported every 0.2 V. Potentials are reported vs. Ag/AgCl. Spectra are scaled to give a maximal absorbance of 1.0 for the de-doped spectrum.

Figure 6.2.4 — GIWAXS patterns for pristine films of A) G3-DEHP and B) G3-DMP coated on Si. Scattering intensities are normalized for film thickness and represented on a linear color scale. The different side chains structures for each polymer are shown.

Figure 6.2.5 — Schematic depiction of contrast matching schemes attempted in NR studies showing A) matching SLD of the
H$_2$O/D$_2$O electrolyte solvent to the NaCl salt, and B) matching SLD of the H$_2$O/D$_2$O electrolyte solvent to the polymer. Panels depict the potential origin of NR contrast for the dry film in air (left), pristine film exposed to electrolyte (middle), and doped films containing ions (right).

Figure 6.2.6 – Diagram of three-electrode cell used for *in situ* NR studies, showing inverted sample orientation with incident neutrons incident to the bottom of the cell. Changes in polymer characteristics, such as thickness ($\Delta d$) and scattering length density ($\Delta$SLD), are depicted, along with the working, counter, and reference electrodes (WE, CE, and RE, respectively).

Figure 6.2.7 – A) CV of G3-DEHP in NaCl/H$_2$O showing potentials used for *in situ* NR. B) Raw NR data for G3-DEHP film under different conditions, offset for clarity. C) Thickness ($d$) and SLD of G3-DEHP extracted from fitting of data in (B).

Figure 6.2.8 – A) CV of G3-DMP in NaCl/H$_2$O showing potentials used for in situ NR. B) Raw NR data for DMP film under different conditions, offset for clarity. C) Thickness ($d$) and SLD of DMP extracted from fitting of data in (B).

Figure 6.2.9 – A) Swelling of G3-DEHP and G3-DMP reported as a percentage change in thickness ($\%\Delta d$) relative to the thickness of the pristine dry film. B) Polymer-electrolyte interfacial roughness ($R_q$) of G3-DEHP and G3-DMP. Thickness and roughness values were extracted from the fitted reflectivity profiles.

Figure 6.2.10 – Schematic of films of de-doped G3-DEHP and G3-DMP after electrochemical conditioning, depicting a greater extent of electrolyte trapping and interfacial roughness/diffuseness for G3-DMP.

Supporting Figure 6.4.1 – Differential pulse voltammograms of (A) G3-DEHP and (B) G3-DMP in 0.5 M NaCl/H$_2$O, showing experimental data (solid lines) and tangents used for determination of $E_{ox}$ (dashed lines).

Supporting Figure 6.4.2 – Cyclic voltammograms ($\nu = 50$ mV s$^{-1}$) showing electrochemical conditioning effect for films of G3-DEHP (A) and G3-DMP (B) on ITO/glass and cycled in 0.5 M NaCl/H$_2$O. Dashed lines correspond to the first CV trace.
of films as-cast. Solid lines correspond to the tenth CV trace, after conditioning.

Supporting Figure 6.4.3 – Cyclic voltammograms of G3-DEHP and G3-DMP films in 0.5 M TBAPF<sub>6</sub>/PC after electrochemical conditioning ($v = 50$ mV s$^{-1}$). Potentials are vs. Ag/Ag$^+$ ($Fc/Fc^+$ $E_{1/2} = +65$ mV).

Supporting Figure 6.4.4 – Potential-dependent C* for G3-DEHP and G3-DMP in degassed 0.1 M NaCl/H<sub>2</sub>O, as determined by EIS performed under an argon blanket and normalized to the dry film volume.

Supporting Figure 6.4.5 – UV-Vis-NIR absorption spectra showing electrochemical conditioning effect for (A) G3-DEHP and (B) G3-DMP films cast onto ITO/glass and cycled 10 times in 0.5 M NaCl/H<sub>2</sub>O. Pristine spectra correspond to data for as-cast dry films prior to any treatment. Potentials for de-doped films are reported vs. Ag/AgCl. Absorption intensities are scaled to a maximum absorbance of 1.0 for the conditioned films.

Supporting Figure 6.4.6 – Sine corrected GIWAXS line cuts for A) G3-DEHP and B) G3-DMP with associated side chain structures.

Supporting Figure 6.4.7 – NR analysis of G3-DEHP on bare Si wafer in air. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.8 – NR analysis of bare Au-coated Si wafer that was used for G3-DEHP studies. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.10 – NR analysis of bare Au-coated Si wafer that was used for G3-DMP studies. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.11 – NR analysis of G3-DEHP on Au-coated Si wafer in air. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.12 – NR analysis of G3-DMP on Au-coated Si wafer in air. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.13 – NR analysis of pristine G3-DEHP film on Au-coated substrate immersed in electrolyte, prior to any electrochemical conditioning. A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.14 – NR analysis of electrochemically condition G3-DEHP film on Au-coated substrate, immersed in electrolyte and held at a de-doping potential of 0.0 V vs. Ag/AgCl. A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.15 – NR analysis of electrochemically condition G3-DEHP film on Au-coated substrate, immersed in electrolyte and held at a de-doping potential of +0.3 vs. Ag/AgCl (slightly oxidized). A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.17 – NR analysis of pristine G3-DMP film on Au-coated substrate immersed in electrolyte, prior to any electrochemical conditioning. A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.18 – NR analysis of electrochemically condition G3-DMP film on Au-coated substrate, immersed in electrolyte and held at a de-doping potential of -0.4 V vs. Ag/AgCl. A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.19 – NR analysis of electrochemically conditioned G3-DMP film on Au-coated substrate, immersed in electrolyte and held 0.0 V vs. Ag/AgCl (after first oxidation wave). A) Schematic of multi-layer model and fit parameters for run,
B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.

Supporting Figure 6.4.20

- NR analysis of electrochemically conditioned G3-DMP film on Au-coated substrate, immersed in electrolyte and held +0.6 V vs. Ag/AgCl (after second oxidation wave). A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), C) SLD depth profile extracted from fit, C) Expansion of low-q region of panel (B) plotted on log-log scale for clarity.

Supporting Figure 6.4.21

- NR analysis of electrochemically conditioned G3-DMP film on Au-coated substrate, immersed in electrolyte and held +0.8 V vs. Ag/AgCl (highest oxidation state) A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), C) SLD depth profile extracted from fit, C) Expansion of low-q region of panel (B) plotted on log-log scale for clarity.

Supporting Figure 6.4.22

- SLD plots resulting from fitting of neutron reflectivity data of A) G3-DEHP and B) G3-DMP immersed in 0.5 M NaCl under different conditions. The curves represent a one-dimensional view of the substrate-polymer-electrolyte heterostructure moving in the positive z direction from the substrate to the electrolyte phase. Gray arrow represents the changes associated with the electrochemical break-in.

Supporting Figure 6.4.23

- Scan rate dependence of CV for G3-DMP film drop-cast on a GC button electrode and cycled in NaCl/H₂O. The current density has been normalized to the scan rate to give a capacitance value.

Figure A. 1

- ¹H-NMR spectrum of compound (2) in CDCl₃.

Figure A. 2

- ¹³C-NMR spectrum of compound (2) in CDCl₃.

Figure A. 3

- ¹H-NMR spectrum of polymer G2-DMP in CDCl₃.

Figure A. 4

- Gel permeation chromatogram of polymer G2-DMP in CHCl₃ at 40°C. Mₙ = 13.4 kDa, D = 1.6 vs. PS.

Figure A. 5

- ¹H-NMR spectrum of compound (4) in CDCl₃.

Figure A. 6

- ¹³C-NMR spectrum of compound (4) in CDCl₃.
Figure A. 7 – $^1$H-NMR spectrum of polymer G4-DMP in CDCl$_3$. 399

Figure A. 8 – Gel permeation chromatogram of polymer G4-DMP in CHCl$_3$ at 40° C. $M_n = 65.9$ kDa, $\mathcal{D} = 2.5$ vs. PS. 400

Figure A. 9 – $^1$H-NMR spectrum of polymer G3-DEHP in C$_2$D$_2$Cl$_4$ (100 °C). 403

Figure A. 10 – Gel permeation chromatogram of polymer G3-DEHP in CHCl$_3$ at 40° C. $M_n = 23.8$ kDa, $\mathcal{D} = 1.5$ vs. PS. 404
# LIST OF SYMBOLS AND ABBREVIATIONS

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<td>° C</td>
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<td>A</td>
<td>Ampere</td>
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<tr>
<td>Å</td>
<td>Angstrom</td>
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<tr>
<td>a*</td>
<td>CIE red-green chromaticity</td>
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<td>Abs.</td>
<td>Absorbance</td>
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<td>AC</td>
<td>Alternating current</td>
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<td>ACN</td>
<td>Acetonitrile</td>
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<td>AFM</td>
<td>Atomic force microscopy</td>
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<td>Neutron scattering length</td>
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(French: International Commission on Illumination)

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<td>CMO</td>
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<tr>
<td>DOE</td>
<td>United States Department of Energy</td>
</tr>
<tr>
<td>DPV</td>
<td>Differential pulse voltammetry/voltammogram</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>E₁/₂</td>
<td>Half-wave potential</td>
</tr>
<tr>
<td>EA</td>
<td>Electron affinity</td>
</tr>
<tr>
<td>Ec</td>
<td>Potential of peak capacitance</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>ECD</td>
<td>Electrochromic device</td>
</tr>
<tr>
<td>$E_{\text{clear}}$</td>
<td>Potential required to reach maximal transmissivity across the visible range (380 – 780 nm)</td>
</tr>
<tr>
<td>ECP</td>
<td>Electrochromic π-conjugated polymer</td>
</tr>
<tr>
<td>EDOT</td>
<td>3,4-Ethylendioxythiophene</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Fundamental band gap</td>
</tr>
<tr>
<td>EG-OFET</td>
<td>Electrolyte-gated organic field-effect transistor</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EO</td>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>$E_{\text{opt}}$</td>
<td>Optical band gap</td>
</tr>
<tr>
<td>$E_{\text{ox}}$ (#1, #2)</td>
<td>Oxidation onset (principal or first, second)</td>
</tr>
<tr>
<td>Equiv.</td>
<td>Molar equivalents</td>
</tr>
<tr>
<td>$E_{\text{red}}$</td>
<td>Reduction onset</td>
</tr>
<tr>
<td>eV</td>
<td>Electronvolt</td>
</tr>
<tr>
<td>F</td>
<td>Farad</td>
</tr>
<tr>
<td>f</td>
<td>Frequency (linear)</td>
</tr>
<tr>
<td>Fc/Fc$^+$</td>
<td>Ferrocene/ferrocenium</td>
</tr>
<tr>
<td>FET</td>
<td>Field-effect transistor</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>$G$</td>
<td>Gate (electrode)</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>$g^*$</td>
<td>Paracrystallinity</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td>GIWAXS</td>
<td>Grazing-incidence wide angle x-ray scattering</td>
</tr>
<tr>
<td>$g_m$</td>
<td>Transconductance</td>
</tr>
<tr>
<td>GMO</td>
<td>Green-Magenta-Orange</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GT</td>
<td>Georgia Institute of Technology</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>i</td>
<td>Current density</td>
</tr>
<tr>
<td>IDE</td>
<td>Interdigitated electrode</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization energy</td>
</tr>
<tr>
<td>$I_G$</td>
<td>Gate current</td>
</tr>
<tr>
<td>$I_{ON/OFF}$</td>
<td>On/off drain current ratio</td>
</tr>
<tr>
<td>$i_p$</td>
<td>Peak current density</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Incident wavevector or beam</td>
</tr>
<tr>
<td>$k_s$</td>
<td>Scattered wavevector or beam</td>
</tr>
<tr>
<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>l</td>
<td>Length (of film or channel)</td>
</tr>
<tr>
<td>$L^*$</td>
<td>CIE Lightness</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Coherence length</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>LR</td>
<td>Liquids Reflectometer</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>MM</td>
<td>Molecular mass</td>
</tr>
<tr>
<td>Mn</td>
<td>Number-average molecular weight</td>
</tr>
<tr>
<td>MOSEFET</td>
<td>Metal oxide silicon field-effect transistor</td>
</tr>
<tr>
<td>Mw</td>
<td>Weight-average molecular weight</td>
</tr>
<tr>
<td>N</td>
<td>Newton</td>
</tr>
<tr>
<td>NA</td>
<td>Avogadro’s constant</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance (spectroscopy)</td>
</tr>
<tr>
<td>Norm</td>
<td>Normalized</td>
</tr>
<tr>
<td>NR</td>
<td>Neutron reflectivity/reflectometry</td>
</tr>
<tr>
<td>OECT</td>
<td>Organic electrochemical transistor</td>
</tr>
<tr>
<td>(iOECT, pOECT)</td>
<td>(interdigitated, planar)</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic field-effect transistor</td>
</tr>
<tr>
<td>OMIEC</td>
<td>Organic mixed ionic-electronic conductors</td>
</tr>
<tr>
<td>ORNL</td>
<td>Oak Ridge National Laboratory</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PA</td>
<td>Polyacetylene</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>PBS</td>
<td>Phosphate buffered saline</td>
</tr>
<tr>
<td>PBTNTT</td>
<td>Poly[2,5-bis(3-tetradecylthiophen-2-yl)]thieno[3,2-b]thiophene</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PMIEC</td>
<td>Polymeric mixed ionic-electronic conductor</td>
</tr>
<tr>
<td>PProDOT,</td>
<td>Poly(3,4-propylenedioxythiophene)</td>
</tr>
<tr>
<td>Poly(ProDOT)</td>
<td>Poly(3,4-propylenedioxythiophene)</td>
</tr>
<tr>
<td>PPV</td>
<td>Poly(para-phenylene vinylene)</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>ProDOT</td>
<td>3,4-Propylenedioxythiophene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>psi</td>
<td>Pounds per square inch</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrene sulfonate)</td>
</tr>
<tr>
<td>PT</td>
<td>Polythiophene</td>
</tr>
<tr>
<td>PXDAT</td>
<td>Poly(3,4-dialkylthiophene)</td>
</tr>
<tr>
<td>PXDOT</td>
<td>Poly(3,4-alkylenedioxythiophene)</td>
</tr>
<tr>
<td>Q</td>
<td>Charge</td>
</tr>
<tr>
<td>q</td>
<td>Momentum transfer vector, scattering vector</td>
</tr>
<tr>
<td>Q_o</td>
<td>Constant phase element (as a circuit element)</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>R</td>
<td>Reflectivity</td>
</tr>
<tr>
<td>R_CT</td>
<td>Charge transfer resistance</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>\textit{R}_q</td>
<td>Root mean square surface roughness</td>
</tr>
<tr>
<td>\textit{rr}</td>
<td>Regioregular</td>
</tr>
<tr>
<td>\textit{R}_s</td>
<td>Equivalent series resistance</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>S</td>
<td>Siemen</td>
</tr>
<tr>
<td>\textit{S}</td>
<td>Source (electrode)</td>
</tr>
<tr>
<td>\text{\textit{s}}</td>
<td>Second</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>SLD</td>
<td>Scattering length density</td>
</tr>
<tr>
<td>SNS</td>
<td>Spallation Neutron Source</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly occupied molecular orbital</td>
</tr>
<tr>
<td>\text{sq.}</td>
<td>Square</td>
</tr>
<tr>
<td>T</td>
<td>Transmittance</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>\text{\textit{TBAPF}}_6</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin film transistor</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>TPA</td>
<td>Triphenylamine</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>\textit{V}_D</td>
<td>Drain voltage</td>
</tr>
<tr>
<td>\textit{V}_G</td>
<td>Gate voltage</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>$V_{ol}$</td>
<td>Volume</td>
</tr>
<tr>
<td>W</td>
<td>Width (of film or channel)</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>$W_o$</td>
<td>Warburg element</td>
</tr>
<tr>
<td>$X_n$</td>
<td>Number average degree of polymerization</td>
</tr>
<tr>
<td>$Y^*$</td>
<td>Complex admittance</td>
</tr>
<tr>
<td>z</td>
<td>Depth in direction of substrate normal</td>
</tr>
<tr>
<td>$Z^*$</td>
<td>Complex impedance</td>
</tr>
<tr>
<td>$Z'$</td>
<td>Real impedance</td>
</tr>
<tr>
<td>$Z''$</td>
<td>Imaginary impedance</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Constant phase element exponent</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Chemical shift (for NMR)</td>
</tr>
<tr>
<td>$\delta'$</td>
<td>Resolution differential</td>
</tr>
<tr>
<td>$\Delta%T$</td>
<td>Change in percent transmittance (contrast)</td>
</tr>
<tr>
<td>$\Delta q$</td>
<td>FWHM of inverse space scattering peak</td>
</tr>
<tr>
<td>$\theta_c$</td>
<td>Critical angle</td>
</tr>
<tr>
<td>$\theta_i$</td>
<td>Incident angle</td>
</tr>
<tr>
<td>$\theta_s$</td>
<td>Scattering angle</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\lambda_{max}$</td>
<td>Wavelength of maximum absorbance</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Carrier mobility</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Potential scan rate</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\tau_z$</td>
<td>Impedance time constant</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Impedance phase angle</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Azimuthal angle (Angle between scattering vector and substrate normal)</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>Goodness of fit</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Ohm</td>
</tr>
</tbody>
</table>
SUMMARY

Among the many applications that capitalize on the electrochemical functionality of π-conjugated polymers, electrochromic devices (ECDs) and organic electrochemical transistors (OECTs) have attracted considerable contemporary interest. The operation of such devices hinges on rapid, reversible electrochemical doping phenomena that effectuate the desired color change in ECDs or conductivity modulation in OECTs. Regardless of the final application of the polymer, these electrochemical doping processes require simultaneous and coupled transport of electrolyte ions and electrons throughout the bulk of the polymeric active layer. The extent and nature of this coupling is intimately tied to a polymer’s chemical composition and structure, electronic properties, complex microstructure, as well as dynamic mass transfer processes occurring across the polymer-electrolyte interface. Understanding relationships between these factors is critical for the rational design of active materials and the ultimate maturation of viable application spaces. This dissertation aims to explore materials design strategies for tuning the optical and electrochemical properties of polythiophene-based active materials in ECDs and OECTs for high-performing, stable electrochemical devices.

To begin, CHAPTER 1 of this thesis provides a brief overview of the fundamental properties of π-conjugated polymers, focusing on their utility in electrochemical devices. CHAPTER 2 then outlines the various experimental methods and techniques used to execute the research described in this work.

In CHAPTER 3, solution co-processing of dioxythiophene-based copolymers is presented as a straightforward and scalable technique for accessing high-contrast black-to-
transmissive electrochromic films with low driving voltages, extended functional lifetimes, and minimal transient chromaticity. This work demonstrates how judicious blend formulation, particularly in the choice of the mid- and high-gap chromophore components, can be leveraged to control the long-term, intermediate, and transient coloration of achromatic, black-to-clear, polymer-based electrochromes for ECDs.

The work presented in CHAPTER 4 and CHAPTER 5 establishes a comprehensive understanding regarding the structural factors governing the properties of two distinct classes of aqueous-compatible OECT active materials—traditional polythiophenes (PTs) and poly(3,4-propylenedioxythiophenes) (PProDOTs). A combination of optical, electrochemical, and x-ray techniques are used to probe the redox response, capacitance, neutral and charged state absorbance properties, solid-state microstructure, and associated device performance of polymers with varying backbones and side chain structures.

CHAPTER 4 investigates the consequences of polar side chain functionalization within a family of aqueous-compatible PTs. The length and substitution pattern of the ethylene glycol-based side chain is found to drastically impact the properties and of the active materials. The redox capacity and stability of these materials can be enhanced simply by changing the side chain distribution along the backbone, even when the overall electroactive mass of the material is reduced. This work demonstrates the balance of material properties that must be achieved for maximal performance.

Meanwhile, CHAPTER 5 shows the properties of polar-functionalized PProDOTs are remarkably less sensitive to the side chain length. These amorphous materials show considerable redox activity in aqueous electrolytes, yet they do not show enhanced steady-
state capacitance or redox stability when compared to the top PT analogue. The work presented CHAPTER 5 also demonstrates how a post-polymerization side chain modification strategy can be used to access an alcohol-functionalized electroactive PProDOT with enhanced redox capacity in saline. The cumulative results of the studies outlined in CHAPTER 4 and CHAPTER 5 indicate that underlying structure-property trends in OECT active materials cannot be generalized across material classes.

Finally, CHAPTER 6 utilizes in situ specular neutron reflectivity to track actuation and aqueous electrolyte uptake by PProDOTs while electrochemically doping. Contrast-matching methods reveal that electrolyte irreversibly penetrates the polymer film, even prior to application of an electrochemical bias, as indicated by changes in film thickness and neutron scattering length density. After repeated cycling, the structure and composition of the films are permanently altered. The extent of potential-dependent reorganization and swelling is found to depend on the side chain functionalization of the polymer. Physical insights provided by the neutron reflectivity shed light on the diffusional limitations associated with the electrochemical doping reaction. Reflectivity models for extracting thickness and compositional changes are presented alongside supporting characterizations highlighting the substantial impact of side chain chemistry on both the steady-state and dynamic redox properties. Such work sets a precedent for using neutron reflectivity to study the volumetric and interfacial characteristics of electrochemically doped conjugated polymers in a more general sense.
CHAPTER 1. INTRODUCTION

This introduction provides a brief overview of the fundamental properties of \( \pi \)-conjugated polymers, with an emphasis placed on their unique electrochemical properties and utility in electrochromic devices and electrochemical transistors. The motivation for each particular research objective in this thesis is provided in the respective chapters. The reader is directed to the references identified in this introduction for a more complete account of the field’s history and recent developments.

1.1 Background of \( \pi \)-Conjugated Polymers

The field of organic electronics has undergone tremendous maturation since the early discovery of conducting polymers in the mid-twentieth century. Since then, a diverse range of synthetic \( \pi \)-conjugated oligomers and polymers have been developed and explored as active electronic and optical components in photovoltaics,\(^1\),\(^2\) transistors,\(^3\),\(^4\) light-emitting diodes,\(^5\) electrochromic displays,\(^6\),\(^7\) biological sensors,\(^8\),\(^9\) supercapacitors,\(^10\) and actuators,\(^11\) among other devices. From a technological perspective, organic electronic materials offer several distinct advantages to their inorganic counterparts. Their optoelectronic properties can be tuned via well-established chemistries, allowing for material properties to be readily and predictably tailored for device applications. Moreover, these materials can be functionalized with aliphatic or polar solubilizing groups and consequently dissolved and processed as electronic inks in low-cost, scalable processing schemes. From a fundamental perspective, \( \pi \)-conjugated materials also serve as stimulating systems for basic scientific research, where they have facilitated the development new models to describe carrier transport,\(^12\),\(^13\) electronic structure,\(^14\),\(^15\) charge separation,\(^16\),\(^17\) and ion-electron coupling.\(^18\),\(^19\)
In these contexts, c such as polyaniline (PANI), polythiophene (PT), poly(paraphenylene vinylene) (PPV), polypyrrole (PPy), and derivatives thereof have remained at the forefront of organic electronics research. The underlying optoelectronic, electrochemical, and physical properties of these so-called “plastic electronics” have been extensively studied and leveraged to develop lightweight, flexible, and even wearable electronics.\textsuperscript{20–22}

1.1.1 Conjugation Length and Band Theory

A defining characteristic of all π-conjugated materials, whether oligomeric or polymeric, involves extended delocalization of π bonding electrons across overlapping p\textsubscript{z} orbitals, which are positioned normal to the nuclear plane. This bridging of p\textsubscript{z} orbitals across neighboring sp\textsuperscript{2} hybridized atoms (usually carbon) commonly arises in the presence of alternating single and double bonds. Similar patterns of orbital mixing and conjugation can also be achieved in any contiguous systems of p\textsubscript{z} orbitals, including those incorporating anionic (or cationic) species with full (or empty) p\textsubscript{z} orbitals. In these cases, net molecular charge can be distributed across the molecule through the delocalized p\textsubscript{z} orbitals.

The emergence of a band-like electronic structure in a conjugated polymer can be understood using polyacetylene, (C\textsubscript{2}H\textsubscript{2})\textsubscript{n}, as an ideal model of a simple conjugated polymer with one-dimensional periodicity.\textsuperscript{23} The p\textsubscript{z} atomic orbitals from each carbon atom linearly combine to form stabilized and destabilized molecular orbitals (π bonding and π* antibonding, respectively).
Figure 1.1.1 – Simplistic depiction of orbital energy level evolution in polyenes, showing energy (E) vs. the number of π bonds. A band-like structure with increasingly small (yet finite) band gap ($E_g$) evolves for increasingly long polyenes. The HOMO and LUMO are labeled and shown for ethylene.

As shown in Figure 1.1.1, as the number of π bonds in the polyene carbon chain increases, the highest-occupied molecular orbital (HOMO) is progressively destabilized, while the lowest unoccupied molecular orbital (LUMO) is progressively stabilized. Simultaneously, discrete bonding and antibonding π molecular orbitals overlap and form frontier energetic bands: an occupied valence band (VB) and an unoccupied conduction band (CB).24 Energy levels within the VB are sufficiently close that excitations within these bands can be accomplished through thermal fluctuations alone. In this band regime, the energetic difference between the top of the valence band (HOMO) and bottom
of the conduction band (LUMO), herein referred to as the fundamental band gap $E_g$, decreases as a function of polyene length. It should also be noted that this gap is finite, even in the theoretical limit of infinitely long over-lapping $\pi$ systems, due to the geometric and electronic consequences of Peierls distortion.$^{25}$

1.1.2 Optoelectronic Consequences of $\pi$-Conjugation

The extended network of $\pi$ electrons in conjugated polymers gives rise to unique optoelectronic properties that differentiate conjugated polymers from conventional macromolecules. The $E_g$ of conjugated polymers is relatively small (1-4 eV), giving rise to semiconducting transport behavior. Furthermore, the evolution of the electronic states into band-like structure allows for the injection of mobile charge carriers into the $\pi$ system and facile (electro)chemical oxidation/reduction. Because of these properties, conjugated organic materials have been found to be useful in a range of solid-state electronic and electrochemical applications.

Correspondingly, the optical band gap $E_{opt}$ is also small, as it is related to $E_g$. Therefore, electronic transitions of conjugated polymers (like polyacetylene) often occur within the visible range of light, as opposed to electronic transitions in conjugated oligomers (like 1,3-butadiene) which occur in the ultraviolet region. Therefore, many conjugated polymers can be vibrantly colored and/or exhibit visible photoluminescence characteristics. Combined with their electronic features, these unique optical properties have allowed the development of light-emitting diodes, photovoltaics, fluorescent sensors, and electrochromic devices all derived from conjugated organic materials.
1.1.3 Charged States in π-Conjugated Materials

In accordance with the orbital hybridization described previously, a conjugated polymer has a greater electron affinity ($E_A$) and lower ionization energy ($I_E$) than the analogous conjugated oligomers. Accordingly, the material can be easily oxidized or reduced via chemical or electrochemical means. Faradaic charge transfer between the conjugated polymer and an electrode or an oxidizing/reducing agent introduces charges (electrons or holes) into the π system of the polymer backbone. Similarly, charge carriers can be introduced electrostatically through charge injection by the field effect, as in organic field-effect transistors (OFETs). Free carriers in the π system may also be generated as the result of exciton dissociation in neat semicrystalline conjugated polymer films due to energetic heterogeneity and also by via acid-base chemistries. The introduction of these charges along the polymer backbone, also called “doping,” is coupled to significant changes in a polymer’s optoelectronic properties, chain conformation, density of states, and extent of energetic disorder. These charged states exhibit unique spectral characteristics. Notably, doping of conjugated polymers is commonly associated with a non-linear enhancement of charge carrier mobility such that remarkably high overall conductivities (up to $\sim10^3$ S/cm) may be achieved. The different mechanisms of doping and the practical utility of doped conjugated polymers will be further described in CHAPTER 1.1.4.

Charges introduced in delocalized π systems can act as mobile carriers and contribute to the overall electrical conductivity of the material. Stabilized carriers may be positive (holes) or negative (electrons), in so-called “p-type” and “n-type” materials—terminology adapted from conventional semiconductor physics. Weakly bound π electrons
(or electron holes) can move along constituent chain segments or between chains that have sufficient $\pi$ orbital overlap. The physical and mechanical properties of solid conjugated polymer assemblies are largely governed by van der Waals interactions, giving rise to significant structural disorder that influences charge carrier (de)localization and transport. The mechanism of this transport is highly dependent on the dimensionality of the carrier wave function, Coulomb interactions, and the extent of charge-lattice interactions.\textsuperscript{24,36–39} Electronic charges are strongly coupled to their surrounding nuclear geometry, which introduces addition complexities in understanding and predicting carrier evolution, stabilization, coupling, and mobility.

The model polymer described in CHAPTER 1.1.1, \textit{trans}-polyacetylene (PA), exhibits unique charge carrier properties due to the degenerate nature of its ground state (i.e., the exchange of single- and double-bonds produces identical ground state geometries). In this material, a so-called “soliton” defect creates a mid-gap state that can be singly occupied in the case of neutral PA, and empty (or doubly occupied) in the case of a positive (or negative) carrier.\textsuperscript{14,24}

The research described herein focuses on p-type polythiophenes (PTs) and derivatives thereof, which unlike PA, have a non-degenerate ground state. In the case of PTs and similar poly(heterocycles), exchange of single- and double-bonds in these materials produce energetically non-identical nuclear geometries. The introduction of charge carriers causes a transition from an aromatic/benzenoid structure to a quinoidal structure with a higher total energy. In such quinoid structures, inter-ring bonds adopt more double-bond character, as shown for the repeat unit of poly(3,4-ethylenedioxythiophene)
(PEDOT) in Figure 1.1.2. In all cases, the quinoid structure has a lower IE than the corresponding aromatic structure.

Figure 1.1.2 – Early theoretical understanding of the electronic structure of polaron and bipolarons in PEDOT, a conjugated polymer with a non-degenerate ground state. Allowed and forbidden optical transitions are shown as solid and dashed arrows between the valence band (VB), conduction band (CB), and other induced states. The corresponding transitions are represented on an optical absorption spectrum. For simplicity, only three repeat units of the polymer are shown undergoing oxidation and geometric reorganization. Figure has been adapted with permission from cited literature and modified for clarification. © 2003 American Physical Society.
In traditional descriptions of p-doping in these systems, removal of a π electron causes the formation of a polaron, which is a charge accompanied by a local geometric reorganization to a more quinoidal structure. Polaron formation is accompanied by the formation of a mid-gap state occupied by the remaining single, unpaired electron.\textsuperscript{14,24} Thus, these polaronic quasi-particles are carriers with electronic spin. In the polaronic state, two lower-energy electronic transitions exist (labeled P1 and P2, as shown in Figure 1.1.2), giving rise to new optical transitions in the near infrared (NIR) and diminished absorption in the visible, as the neutral species is depleted.\textsuperscript{40} When more electrons are removed from the backbone, polarons combine to form bipolarons, which are spinless charge carriers with no unpaired electrons. To form bipolarons, there is a competition between the Coulombic repulsion of bringing two like charges together and the energetic benefit of minimizing the higher energy quinoidal geometry. Ultimately, an energetic balance is achieved, which usually results in a bipolaron delocalized over 3-4 rings.\textsuperscript{14,24} Moreover, additional bipolaronic mid-gap states are formed, associated with even lower-energy optical transitions (BP\textsubscript{1} in Figure 1.1.2). Upon doping, polaronic and bipolaronic states overlap to form bands to facilitate carrier transport.\textsuperscript{14} It should be noted that while conventional models depict fully doped (bipolaronic) PEDOT with a quinoidal geometry (as portrayed in Figure 1.1.2), some resonant Raman studies on PEDOT have suggested conflicting results surrounding the molecular geometry of these highly doped states, suggesting that PEDOT may actually re-adopt an aromatic geometry at very high doping levels.\textsuperscript{41,42}
Figure 1.1.3 – Electronic structures of allowed absorption transitions in a p-doped conjugated polymer depending on doping level, showing the neutral π-π* transition (N), polaronic transitions (P1, P2), bipolaronic transition for an idealized single chain (BP), and transitions associated with a polymer assembly with a high concentration of polarons and bipolarons (intra- and inter-chain bipolaron bands). B) Representative absorbance spectra for the illustrated transitions. This original figure is derived from interpretations presented in the literature\cite{15,43} and the thesis of Dr. Dylan Christiansen.\cite{44}

Early models to describe charge carriers and their optical signatures in organic electronics were pioneered largely by J.L. Bredas,\cite{14,25,45-47} and these models have served as excellent descriptions for understanding charged states in π-conjugated polymers. More recently, however, there have been revisions to this model to better account for results of
experimental studies (especially those utilizing ultraviolet photoelectron spectroscopies) and new time-dependent density functional theory (DFT) calculations. These models account for on-site and inter-site Coulomb interactions and proposes a new evolution of the band structure for both p- and n-type materials, as shown in Figure 1.1.3. Such descriptions involve a fundamental re-ordering of the frontier energy levels. In the case of p-doping, introduction of a positive charge on the polymer backbone causes the singly-occupied molecular orbital (SOMO) and the new HOMO’ levels to depress below the level of the original HOMO as a result of on-site coulomb interactions. In this picture, both frontier levels are stabilized, an unoccupied intragap state or band (SOMO*) with spin restrictions emerges, giving rise to P1 and P2 transitions (Figure 1.1.3). This is in contrast to earlier models, which posit that the half-occupied SOMO level associated with the polaron forms within the gap and that neighboring neutral species remain unaffected. These refined polaron models are consistent with recently reported transient absorption spectroscopy, but there still remains disagreement and some uncertainty regarding the interpretation of these data. Moreover, inconsistency persists in terms of understanding the formation of and spin associated with charged states, as recently illustrated for several PEDOT derivatives. Given the complex nature of interacting charges in these materials as well as the structural variety encountered, it may come as no surprise that developing a comprehensive model to describe carriers has been a longstanding challenge.

1.1.4 Doping of π-Conjugated Polymers

Despite the uncertainty surrounding the electronic structure of charge states in conjugated polymers, these charge states are essential to the functionality of these...
materials. As mentioned earlier, charge carrier introduction (doping) can be accomplished in a number of ways. Chemical doping involves treating the active material with a chemical oxidant (or reductant) that removes (or donates) an electron, thus introducing a hole (or extra electron) into the π system, which is then stabilized by the counter-ion of the dopant. When utilizing chemical dopants, partial and integer charge complexes can form, each with different effects on the final charge transport properties of the polymer.\textsuperscript{53} Often, the doping reaction is not dictated by electron-transfer thermodynamics but also by interfacial or mass transport limitations, such as the dopant-polymer compatibility, the extent to which the dopant can intercalate into the polymer, and how well the stabilizing ion can “dock” next to the induced charge.\textsuperscript{54,55} Consequently, chemical doping is frequently not very well-controlled. Beyond molecular oxidants and reductants, doping can also be accomplished through acid-base reactions by treating a conjugated polymer with a protic acid.\textsuperscript{29} Doping of PAN-I is typically done using acid-base chemistry that (de)protonates the backbone nitrogen atoms.\textsuperscript{30}

In OFETs, polarization of a dielectric by a gate electrode results in field-effect (or electrostatic) doping of an organic semiconducting active layer. Here, there are no Faradaic electron transfer reactions; rather, dipoles formed in the dielectric induce the formation of charge carriers within the first few nanometers of the semiconductor-dielectric interface, thus doping the polymer and turning the transistor “on.” Doping, and therefore mobility and conductivity modulation, occurs within this shallow region of the polymer film, where the structure of the polymer remains otherwise physically and mechanically undisturbed. In lieu of an insulating dielectric, electrolytes may also be used to facilitate doping. In such so-called electrolyte-gated OFETs, or EG-OFETs, the organic semiconductor is assumed
to be impermeable to ions in the surrounding electrolyte. Electric double layer charging at the polymer-electrolyte interface facilitates electrostatic doping via charge accumulation. Due to the large capacitance of the gating electrolyte, EG-OFETs can exhibit higher carrier densities at lower gate voltages when compared to traditional OFETs.\textsuperscript{56}

Finally, conjugated polymers can be doped through electrochemical means. Such configurations typically involve a conjugated polymer fully or partially adsorbed to an electrode and immersed in a liquid electrolyte. In response to a bias applied between the polymer-coated electrode and a reference/gate electrode, electrons from the entire depth of the polymer film may be faradaically injected into and/or removed from the $\pi$ system. These carriers, in combination with mobility changes that occur upon doping, are thought to be responsible for the enhanced conductivity observed for electrochemically doped systems. The mode of carrier transport in electrochemically doped CPs is a bit ambiguous, with evidence for both mixed valence conduction and more band-like, bipolaronic transport existing.\textsuperscript{57,58}

As mobile charges are injected into the polymer film, solvated counter-ions from the electrolyte migrate into the bulk of the polymer film and stabilize these charged states. Some work has been suggested that the amount of electrolyte transported into the film exceeds that required for charge neutrality, thus facilitating capacitive-like charging of various interfaces (e.g. the buried polymer-electrode interface or internal structural interfaces within the polymer film itself).\textsuperscript{19,59–61} Evidence both for and against the existence of a simultaneous double layer charging at the polymer-electrolyte interface exists.\textsuperscript{57,61–63}
The diverse observations relating to carrier transport and capacitive coupling may largely be the result of the various polymer structures (and therefore properties), film microstructures, electrolytes, bias conditions, and techniques that are combined to study electrochemical doping.

Upon application of a reverse bias, the polymer may be de-doped via the reverse redox process and returned to its neutral state. De-doping is accompanied by counter-ion transport (either expulsion or uptake) to maintain electroneutrality within the bulk of the film. Electrochemical doping of π-conjugated polymers and the utility thereof will be further described in CHAPTER 1.3.

1.2 Structural Control of Optoelectronic Properties

One of the unique benefits of organic electronic materials is their structural versatility and tunability. Modification of π-conjugated materials at the molecular and atomistic level often results in substantial changes in their macroscopic optoelectronic, electrochemical, physical, and mechanical properties. Thus, straightforward organic chemistries can be leveraged to readily prepare conjugated polymers with highly targeted properties for a range of different applications. Since its inception nearly half a century ago, the field of organic electronics has made incredible progress understanding, predicting, and implementing structure-property interrelationships for engineered plastic electronics. Here, a brief overview of some of these basics concepts is presented. For a more detailed or supplemental survey of these concepts, the reader is directed to more thorough textbook chapters.\textsuperscript{64–70} theses.\textsuperscript{44,71–74} and articles.\textsuperscript{75–78}
1.2.1 Electronic and Steric Influences

Structural changes in both the parent π-conjugated backbone and the substituent groups appended to the polymer backbone can induce various notable bulk changes in a material’s properties. Modification of the polymer backbone with functional groups that increase or decrease the π electron density of the backbone through resonance effects of can (de)stabilize molecular orbitals, thereby modifying the band structure and giving rise to different electronic characteristics and optical absorption features.\textsuperscript{65} In the absence of any competing steric interactions (which are explained later in this section), derivatization of the backbone with π electron donors or acceptors leads to a reduction in band gap.\textsuperscript{79} For instance, covalent functionalization of the backbone with π donors like ether, thioether, and amino groups significantly destabilizes the molecular HOMO (or valence band) while destabilizing the LUMO (or conduction band) to a lesser degree. Analogously, incorporation of π withdrawing groups like cyano or ester moieties significantly stabilizes the LUMO (or conduction band) while only stabilizing the LUMO (valence band) marginally.\textsuperscript{79} Copolymerization of electron-rich (donor) and electron-poor (acceptor) groups in so called donor-acceptor (DA) polymers results in further orbital hybridization and charge transfer-like optical transitions.\textsuperscript{78,80,81} In polymers with aromatic repeat units (e.g. polyphenylene, polyheterocycles), the aromatic character of the constituent arene can substantially change the energetic landscape and corresponding optoelectronic properties.\textsuperscript{82} The strength of the π donation imparted by the heteroatom in a polyheterocycle plays a crucial role in determining the amount of intrinsic conjugation between rings and dictating the properties of the material. These principles explain the differences between polymers like PT and PPy, which have different values of IE, EA, and $E_g$. 
Beyond the direct electronic modifications described above, steric effects also play a large role in determining the macroscopic properties of a conjugated polymer. In particular, sterically interacting heterocycles or substituent groups can increase torsional disorder along the polymer chain, reduce the degree of π orbital overlap among adjacent repeat units, increase the band gap, and raise the IE of the material. Such steric influences can also obstruct interactions between cofacial chromophore segments, influencing the microstructural, optical, and electronic properties in solution and the solid state. In redox applications, steric interactions raise the IE and lower the EA of the polymer by obstructing planarization of the polymer to its quinoidal form upon oxidation or reduction. Repeat units comprised of fused ring systems and sterically non-interacting substituent groups can induce chain planarity and promote interactions of neighboring chromophores. Other chemical functionalities, such as hydrogen bonding and non-covalent heteroatomic effects, are thought to induce interactions between or within a polymer chain to enhance or suppress chain planarity, which in turn can influence relevant properties, such as carrier mobility, energy levels, chain conformation, and/or polymer crystallinity.\textsuperscript{83–86}

1.2.2 Development of Poly(3,4-dioxythiophenes)

Among the many structurally diverse conjugated polymers that have been reported in the literature, PTs remain one of the most widely studied class of conjugated polymers.\textsuperscript{87} In PTs, derivatization of the thiophene β positions with alkyl substituents affords poly(3,4-dialkylthiophenes) with enhanced solubility and greater steric interactions between repeat units. The commonly studied polymer poly(3-hexylthiohpene) (P3HT) is a monosubstituted PXDAT analogue. Further derivatization of the thiophene β positions with two alkyloxy substituents affords poly(3,4-alkylenedioxythiophenes) (PXDOTs) with
enhanced electron richness. An early derivatization of such materials with one methoxy group per thiophene yielded poly(4,4’-dimethoxybithiophene) which, based on the authors’ claims, was able to be oxidized to a doping level corresponding to one charge per thiophene ring due to its enhanced electron richness.  

One of the most popular PXDOT is PEDOT, a polymer first prepared by Bayer in the 1980s and later reported by Jonas et al. PEDOT consists of the two alkoxy substituents joined by an ethylene bridge, yielding a bicyclic repeat unit (Figure 1.2.1). Not only does the disubstitution of the oxygen groups in PEDOT lower the IE and band gap when compared to the standard PT, but through-space S-O heteroatom interactions between neighboring repeat units are thought to also help planarize the backbone of PEDOT, further promoting π orbital overlap. Furthermore, the disubstitution at the β position is thought to sterically protect the PEDOT backbone during oxidative polymerization and electrochemical cycling. This renders disubstituted polymers more stable when compared to un- or mono-substituted analogues like PT or PPy, which are susceptible to side reactions at unprotected β positions, resulting in “overoxidation,” cross-linking, and/or degradation of the π system. Since its discovery, PEDOT has become a centerpiece of conjugated polymer research due to its stability, high transmissivity in the doped state, impressive conductivity, and redox properties.

Derivatives of PEDOT have since been developed to impart superior solubility tune its optoelectronic and electrochemical properties. A notable example that will be discussed extensively in this thesis is poly(3,4-propylenedioxythiohpene), or PProDOT (Figure 1.2.1). This material, which was first reported in the 1990s, features a propylene bridge joining the two oxygen substituents. Thus, the central carbon of the propylene bridge can be tetrahedrally and symmetrically substituted with different functionalities, allowing for
the development of a wide range of stable electroactive polymers with various solubilities, conductivities, functionalities, optoelectronic properties, and redox characteristics (especially in the field of electrochromism, as will be discussed later). While ProDOT has a seven-membered ring fused to the backbone compared to PEDOT’s six membered ring, a substituted biProDOT dimer is actually expected to be just as planar as a biEDOT dimer, as shown by their similar through-space resonance stabilization. The dimers do differ, however, in the extent of π-donation from the oxygen lone pairs into the conjugated backbone. The 6-membered ring in EDOT is thought to orient oxygen substituents in a manner that is more amenable to π-donation than the corresponding 7-membered ring in biProDOT, resulting in more than twice the resonance stabilization for the oxygen lone pair in the biEDOT analogue.

![Repeat unit structures of representative polythiophene derivatives: PT, PXdAT, PXDOT, PEDOT, and PProDOT.](image)

**Figure 1.2.1 – Repeat unit structures of representative polythiophene derivatives: PT, PXdAT, PXDOT, PEDOT, and PProDOT.**

### 1.3 Electrochemical Functionality

Electrochemical doping of π-conjugated polymers is an intricate process involving many simultaneous, sometimes competing, processes (Figure 1.3.1). Upon doping/de-
doping, solvent and counter-ions must move in and out of the polymer film, which can cause substantial volumetric changes and/or reorganization of the active polymer layer. Accompanying this ionic transport, transport of electronic charge carriers (electrons/holes) must also occur simultaneously through the bulk of the film and transferred at the polymer/electrode interface to effectuate the redox reaction. The doping process is also associated with substantial changes in charge carrier mobility. Considering the simultaneous and coupled transport of ionic and electronic charged species, redox active conjugated polymers are commonly referred to as polymeric or organic mixed ionic-electronic electronic conductors (PMIECS or OMIECs).\textsuperscript{18,105}

Figure 1.3.1—Electrochemical p-doping of an arbitrary conjugated PXDOT, showing transition from a neutral aromatic geometry to bipolaronic quinoidal state, electron removal at the polymer-electrode interface, and net anion migration into the film.
To electrostatically stabilize electronic charge carriers, electrolyte counter-ions must penetrate the polymer film. Considering the diverse and often competing factors that influence ionic and electronic transport, and the coupling thereof, electrochemical doping can be difficult to understand and design in a predictable manner. The structure-property interrelationships governing the effective electrochemical doping of conjugated polymers and the application thereof will be the central focus of this work.

The reversible redox properties of \( \pi \)-conjugated polymers have attracted interest among many technical communities. Because electrochemical doping effectuates changes in a film’s ion composition, electronic potential landscape, carrier density, mobility, mechanical properties conductivity, optical properties, and thickness, conjugated polymers have been pursued as active materials in a plethora of redox applications, including optical devices (electrochromic displays, light-emitting electrochemical cells), electrochemical transistors (for sensors, neuromorphic computing, and circuitry), bio-electronic devices (ion pumps, drug delivery, neural probes, and artificial muscles), switchable surfaces, and energy storage devices. This work will focus on conjugated polymers with properties targeted toward two ultimate applications – electrochromic devices (ECDs) and organic electrochemical transistors (OECTs).

1.3.1 Conjugated Polymer-Based Electrochromic Devices

Electrochromism is a phenomenon in which a material changes color upon application of an external bias. Commercially, electrochromic materials are employed in dimmable automotive mirrors, IR-filtering architectural windows, and low-power
reflective displays. Commonly used electrochromes, such as metal oxides and viologens, can suffer from slow switching kinetics, limited color space, large current or voltage requirements, or energy-intensive processing.

Because neutral and charged states in π conjugated polymers exhibit distinct optical signatures (CHAPTER 1.1.3, Figure 1.1.3), these polymers are an attractive alternative class of electrochromic materials. Electrochromic π-conjugated polymers (ECPs) can undergo full colored-to-colorless transitions on rapid time scales (often within second to sub-second regimes), with high coloration efficiencies, excellent contrast (Δ%T at $\lambda_{\text{max}}$ up to 75%), notable bistability, and facile processability if modified with appropriate solubilizing groups.\textsuperscript{122,123} ECPs have also been successfully integrated into plastic\textsuperscript{124} and paper-based\textsuperscript{125,126} electrochromic displays, making them promising candidates for lightweight and flexible and devices. The following sections will give a brief overview of the fundamental aspects of ECPs and polymer-based ECDs.

1.3.1.1 Fundamentals of Materials and Devices

ECPs can be cathodically or anodically coloring, depending on whether the material’s colored state corresponds to its cathodic or anodic state. Common cathodically coloring ECPs include PProDOT derivatives and donor-acceptor polymers that transition between vibrant hues (absorbing visible light) and highly transmissive positively charged (p-doped) states that absorb in the IR. Because the colored state of PProDOTs is the more reduced (cathodic) species, PProDOTs are deemed cathodically coloring. Anodically coloring materials, such as triphenylamine (TPA) derivatives have also been studied. Both the ProDOT-based polymers described above and TPA electrochromes are materials that
switch between a neutral and oxidized state, and therefore both are p-type electrochromes. However, the neutral spectra of TPA-based polymers are significantly blue-shifted due to the shorter effective conjugation lengths associated with the cross-conjugated TPA core. As a result, neutral TPA polymers often absorb in the UV and appear highly colorless or yellow. Upon oxidation, TPAs absorb across the visible spectrum, thus they are classified as anodically coloring electrochromes.

The work discussed in in this thesis will focus on cathodically coloring p-type ECPs derived from ProDOT repeat units. An example of a polymer-based ECD is depicted in Figure 1.3.2. The device is assembled with a battery-like design, with a transparent electrolyte sandwiched between two conducting and transparent electrode substrates. One electrode is coated with the active ProDOT-based ECP (“Electroactive polymer 1”), while the other is coated with a secondary charge-storage material usually comprised of another redox-active polymer that does not undergo visible color changes (“Electroactive polymer 2”). In the discharged state, the optically active ECP is in its cathodic and colored state, while the charge-storage polymer in its anodic state and imbibed with electrolyte anions. Upon charging, the ECP layer oxidizes to its transmissive form, up-taking anions from the electrolyte to stabilize its charged state. Simultaneously, the secondary layer is reduced to a minimally colored state and expels the stabilizing anions. This process can be repeated for reversible color switching.
1.3.1.1 Color Control in Soluble ECPs

Throughout the past twenty years, a broad range of color-to-colorless ECPs have been developed by tuning the steric and electronic properties of the constituent chromophores.\(^7\) The ProDOT repeat unit has served as a versatile basis for designing many solution-processable polymers with enhanced switching speeds and contrast ratios. Copolymerization of the electron-rich ProDOT with electron-poor repeat units (e.g. benzothiadiazole) yields cyan or green ECPs,\(^80,128\) whereas more deep blue hues be achieved by low-gap, electron-rich ProDOT-EDOT copolymers.\(^101\) Mid-gap ProDOT copolymers can also be tuned by side chain manipulation or copolymerization with other PXDOTs to access pink and purple ECPs with various processing, redox, optical characteristics.\(^6,100,129–132\) High-gap ECPs (e.g. yellow and orange) can be achieved by incorporating repeat units with increased aromatic character (e.g. phenylene),\(^133,134\) installing sterically interacting side chains that distort backbone planarity,\(^135\) or using
repeat units with substantial inherent inter-ring strain.\textsuperscript{104} Accessing an achromatic ECP that switches from a black or gray color to a transmissive state is a bit more challenging and typically requires more nuanced approaches to ECP synthesis and formulation. Strategies targeting color neutral ECPs will be discussed further in CHAPTER 3. For a more comprehensive overview on solution-processable colored-to-colorless ECPS, especially those based on the ProDOT moiety, the reader is directed to several excellent articles and book chapters that chronicle the progress in this field over the last twenty years.\textsuperscript{7,106,123,136,137}

1.3.2 Organic Electrochemical Transistors

The organic electrochemical transistor (OECT), like the polymer ECD, is a device based on the electrochemical doping of $\pi$-conjugated polymers. OECTs represent a class of organic thin film transistors (TFTs) first pioneered in the mid-1980s by Mark Wrighton and colleagues.\textsuperscript{138} The seminal work in the field demonstrated that the conductivity of an electropolymerized PPy thin film channel could be reversibly and electrochemically modulated, acting as a conductivity “switch” across a microelectrode array. Similar phenomena were soon demonstrated with other electropolymerized redox-active conjugated polymers, such as poly(3-methylthiophene),\textsuperscript{139} PA,\textsuperscript{140} PANi,\textsuperscript{141,142} and derivatives thereof.\textsuperscript{143} During this period, electrochemical transistor and transistor-like configurations were primarily used as a method for studying conductivity changes in conjugated polymers. There were some early efforts to use OECTs as either direct sensors for pH,\textsuperscript{144,145} ions,\textsuperscript{146,147} and humidity\textsuperscript{141,148} or as a transducing mechanism for more sophisticated biochemical sensors,\textsuperscript{108,149–153} although the \textit{in vivo} and \textit{in vitro} utility of these
devices was not well-demonstrated. Detailed reviews summarizing some of these applications can be found in the literature.\textsuperscript{154,155}

Interest in OECTs was revived in the 2010s when it became increasingly apparent that conjugated polymers offer highly desirable properties for electronically interfacing with living systems. Many conjugated polymers have elastic moduli commensurate with biological tissue (~kPa–MPa),\textsuperscript{20,156–158} mitigating mechanical mismatch with biological systems. Moreover, the propensity of polar conjugated polymers to swell in aqueous environments allows for the development of conformable and even gel-like electronics.\textsuperscript{8,22} Their potential for facile and low-temperature processing is also considered advantageous, as many biological recognition elements and antibodies used in sensors can denature under extreme processing conditions. Perhaps most notably, the ability of conjugated polymers to support both ion and electron transport is particularly beneficial for developing bio-electronic interfaces. Because biological systems rely on ion fluxes (H\textsuperscript{+}, Ca\textsuperscript{2+}, K\textsuperscript{+}, Na\textsuperscript{+}, and charged neurotransmitters) for signaling, mixed-conducting systems like organic semiconductors offer a unique opportunity to directly transduce biological ionic signals to electronic signals compatible with modern devices.\textsuperscript{159} A number of perspectives and reviews have highlighted the vast opportunities for organic electronic materials as bioelectronic interfaces.\textsuperscript{157,160–164}

Consequently, there has been a growing interest in pursuing OECTs as platforms for biochemical sensors and electrophysiological probes.\textsuperscript{165} OECTs are thought to be capable of extremely large signal amplification with small working voltages (< 1 V). As electrochemical devices, OECTs operate well in ion-rich biological media, where fluids such as saline, saliva, sweat, blood, and urine can potentially serve as the gating electrolyte,
making these devices relevant for point-of-care testing. For the specific detection of biomolecules, the OECT architecture can be modified with enzymes, antibodies, or other recognition elements, yielding sensitive transistor-based sensors. In electrophysiological studies, OECTs have been used both in vitro to directly measure cell activity as well as in vivo for recording electrocardiograms, electroencephalograms, electrooculograms, and electrocorticograms with remarkable signal-to-noise ratios and higher spatial resolution than a polymer-modified electrodes alone. Because the electroactive polymer in the OECT channel can intimately interface with biological systems without the native oxide layer present in inorganic materials used in TFTs, currents can be directly introduced in OECTs for the direct electrostimulation of cells, as well. Recent literature shows that OECTs can be integrated into many form factors, including flexible, fiber-based, printed, implantable, and microfluidic devices, demonstrating their versatility and utility.

1.3.2.1 Working Mechanism of OECTs

The standard architecture for most OECTs resembles that of a typical FET and consists of three terminal electrodes: the gate, source, and drain, as depicted in Figure 1.3.3. The source and drain make contact to the active polymer film, and a source-drain bias (V_D) controls the flow of electronic current through the channel and to the drain (I_D). The channel is contact with an electrolyte, in which the gate electrode is immersed. A bias between the gate and source (V_G) controls the doping level (or redox state) of the polymer and therefore modulates the conductivity of the channel and I_D. Importantly, the redox state of the polymer cannot be established with certainty. In such three-electrode configurations, potentials are referenced to a common metallic source electrode that passes
current throughout device operation. Therefore, conditions in this device cannot be related to any standard electrochemical potential. Some early OECT studies, especially those prior to 1990,\textsuperscript{138,139} utilize a four-electrode configuration that incorporates an electrochemical reference electrode for precise control of the electrochemical potentials applied to the polymer. However, the three-electrode configuration is significantly more prevalent,\textsuperscript{183} especially in many recent application-based reports.

![Schematic of OECT device](image)

**Figure 1.3.3** – Schematic showing the working mechanism of a p-type 3-electrode OECT device with source (S), drain (D), and gate (G) electrodes, operating in a purely electrochemical manner. *Left:* Anions and electrolyte migrate into and swell the film, stabilizing holes ($h^+$) throughout the bulk of the film. *Right:* Mobile holes are injected into the film through faradaic electron ($e^-$) transfer at the polymer-S/D interface.

Regardless of the device architecture (four or three electrode), to achieve the highest conductivity or on-off current ($I_{ON/OFF}$), a large $V_D$ must be applied. For the maximal $I_D$, the magnitude of $V_D$ is often commensurate with $V_G$ (100s of mV) and gradient of redox states exist across the length of the channel,\textsuperscript{184–188} as well as a lateral potential and ion concentration gradient.\textsuperscript{189} This gradient of doping states gives maximum limiting current in the transfer plots,\textsuperscript{185,186,188,190} which is somewhat similar to the “pinch-off” effect
observed in FETs. With this gradient of doping levels (oxidation states) in mind, it is worth pondering about the similarities in so-called mixed valence conduction (e.g. in metallopolymers and radical polymers) and the conduction observed in many electrochemically doped systems,\textsuperscript{57,58,184,190–193} potentially raising interesting points about the different modes of transport in OECT devices.

A defining characteristic of OECT operation involves dynamic ion transport across the polymer-electrolyte interface to facilitate electrochemical doping throughout the bulk of the channel. This is in contrast to EG-OFETs, where ion accumulation at the polymer-electrolyte interface facilitates electrostatic doping only in a thin interfacial region of the channel. In the case of the simplest p-type OECT, holes injected into the polymer film at the $S/D$ contact are compensated by net anion migration into the film (Figure 1.3.3). Meanwhile, the electric field at the gate electrode causes cation accumulation in a double-layer at the gate-electrolyte interface. For simple n-type OECTs, where electrons are the mobile carriers in the channel, the electron injection is compensated by net cation migration into the channel, while anion accumulation occurs at the gate-electrolyte interface. These are the most simplistic cases, and more complicated systems exist where there can be mixed cation/anion transport or faradaic processes occurring at the gate electrode.

Depending on the composition and structure of the channel, doping may occur through different or unique means. For instance, (de)doping of PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), a p-type channel material, is facilitated by net cation transport. Holes in PEDOT are stabilized by the PSS polyanion immobilized in the channel. Therefore, the redox process is dominated by the net migration of mobile electrolyte cations, which can stabilize uncompensated PSS\textsuperscript{−} sulfonate groups depending
on the oxidation state of PEDOT. Similar charge stabilization occurs in conjugated polyelectrolytes with covalently tethered ionic groups that can facilitate doping. In addition, it has been postulated that most active materials actually operate via a mixture of bulk electrochemical doping and interfacial field-effect doping, as opposed to purely one mechanism.\textsuperscript{194} The relative contribution of each is thought to depend on the polymer microstructure, the magnitude and frequency of $V_G$, and specific polymer-electrolyte interactions.\textsuperscript{194–196}

The volumetric electrochemical doping processes described above imposes interesting device-level ramifications. First, OECTs have relatively limited operational bandwidths. Because device switching requires tortuous ion migration through the entirety of the channel, OECTs operate at much slower speeds than EG-OFETs, which rely on rapid double-layer charging (up to \(~0.5\) kHz vs. \(~\text{MHz}\), depending on geometry).\textsuperscript{63,183} In some systems, it is even possible to change the mechanism of doping from EG-OFET to OECT simply by increasing the operating frequency.\textsuperscript{195} Secondly, the channel of an OECT has a much higher functional capacitance than the channel of a typical FET. Consequently, OECTs are thought to support larger $I_D$ in response to small fluctuations in $V_G$ when compared to OFETs. Therefore, OECTs are thought to be capable of large signal amplification.\textsuperscript{183} It is important to note this signal amplification has been the subject of recent debate in the literature. Some researchers in the field of electrolyte-gated transistors posit that the degree of signal amplification in OECTs cannot be precisely ascertained and, in fact, actually may not outperform EG-OFETs.\textsuperscript{197,198}
1.3.2.2 Describing Device Behavior

There have been numerous attempts to quantitatively describe the device physics of OECTs and model their transient and stead-state characteristics. Part of the difficulty in this task lies in the fact that OECTs are fundamentally electrochemical devices, but parallels can be drawn to the characteristics and functionality of solid-state MOSFETs. Early work by Pickup and Robinson relied on electrochemical analyses to describe and predict OECT device characteristics.\textsuperscript{184,188,190} Later, OECT device models were developed based on conventional MOSFET behavior.\textsuperscript{199,200} These models were largely pioneered by Bernards and Malliaras, who described the steady-state behavior of OECTs in terms of a three-dimensional volumetric capacitance ($C^*$) of the channel, as opposed to the two-dimensional dielectric capacitance in MOSFETs. A critical aspect of this model is that the ionic and electronic circuits are represented by two perpendicular circuits coupled by a single gate capacitance which dictates the concentration of ions within the channel. These models which were later further developed by colleagues of Malliaras, such as Rivnay and Friedlein,\textsuperscript{201,202} were predominantly based on OECTs comprising PEDOT:PSS active layers. Further discussion on $C^*$ measurements, especially for understanding OECT operation, will be discussed later in CHAPTER 2.3.4.4.

The maximum transconductance, $g_m$, is commonly seen as the figure-of-merit for OECT device performance. This quantity is related to the amplification of $I_D$ in response to $V_G$, thus capturing the overall sensitivity of the transistor. The mainstream OECT community has proposed a quantitative description of $g_m$, which can be found in Equation 1. Here $W$, $d$, and $l$ correspond to the channel width, thickness, and length, respectively),
threshold voltage $V_T$, as well as the mobility ($\mu$) and volumetric capacitance of the channel material.

$$g_m = \frac{\partial I_D}{\partial V_G} = \frac{W \cdot d}{l} \cdot \mu \cdot C^* \cdot (V_T - V_G)$$

(1)

The implication of Equation 1, as it is described in numerous reports,\textsuperscript{183,201} is that the performance of an OECT proportionally scales with the geometry of the channel and the product of the mobility and capacitance of the channel material. Thus, the product $\mu C^*$ has been hypothesized to be a “nominally geometry and bias-independent” material figure-of-merit for OECTs.\textsuperscript{201} The results of several studies have supported this notion.\textsuperscript{201,203}

With this in mind, there are several aspects worth consideration. First, the concept of a volume-independent $C^*$ may not be generalizable for all materials and experimental configurations, as described later CHAPTER 2.3.4.4 starting on pp. 87. Secondly, extracting material properties from device measurements can be a tenuous practice. Device characteristics may not only depend on the on geometry of channel, but also on the composition and placement of the gate electrode gate, configuration-specific contact resistances, and parasitic capacitive charging. For instance, there has been a few reports in the literature showing how contact resistance, especially at the polymer-electrode interface, can have substantial influence on OECT device characteristics, leading to trends deviating from those predicted by Equation 1.\textsuperscript{204–207} These contact resistance effects depend not only on the chemical structure of the active material, but also on the doping level (redox state) of the channel, the polymer-electrode overlap area, and the channel length.\textsuperscript{204,205,208} In a recent study, modification of gold source and drain electrode with alkane thiol self-assembled monolayers was shown to improve the interfacial compatibility of the polymer
and underlying electrode, thereby reducing the contact resistance in the device and resulting in a three-fold enhancement of transconductance.\textsuperscript{206} This result calls into question how reliably the device characteristics actually predict inherent material properties. In fact, few OECT studies conduct transmission line measurements to extract and correct for potential- and structure-dependent contact resistance. Such contact resistance effects also manifest in widely used “electrochemical \textit{in situ} conductance” measurements of conducting polymers,\textsuperscript{209} where contact resistance is not commonly controlled, measured, or accounted for in many studies. In other types of organic transistors, like OFETs, there has also been studies to account for contact resistance effects to better compare channel materials,\textsuperscript{210–216} demonstrating how important these properties are for other types of organic TFTs. Despite the seemingly widespread awareness of these issues in the organic transistor community, it is interesting that contact resistance effects are often not explicitly measured in studies that report and benchmark new OECT materials. Thus, meaningful comparison of materials based solely on device characteristics can be difficult, especially when these devices are fabricated in different labs and measured with different metrology.

Moreover, many implicit assumptions in these modes do not hold true for conjugated polymers, such as the dependence of carrier mobility with gating potential, the latter diffusion of later ions, etc. While there have been some attempts to refine these models,\textsuperscript{189,204,208,217} it remains unclear how robust such descriptions are across material systems. Evaluation of such models generally requires highly controlled device geometries, careful patterning of active materials,\textsuperscript{218} and rigorous minimization of all parasitic capacitances and resistances.\textsuperscript{202,204} Therefore, without adequate engineering of electrical and device-level engineering, the significance of the resulting device data can vary. In
addition, later potential gradients, ion drift, and doping states across the length of the transistor channel causes transistor behavior that significantly deviates from model predictions. This was highlighted in several recent papers by the group of Björn Lüssem, who underscore the need for a more complete descriptions of the processes and parasitic resistances and the polymer-electrode interfaces to better understand OECT device operation and geometry scaling. In 2020, Tu and Fabiano provided a comprehensive overview of OECT device physics based on the drift-diffusion model and recounts the evolution of device descriptions within the past several decades. A related drift-diffusion model was used by Tybrandt et al. in 2019 to describe current-voltage characteristics of common CPs. Moreover, there is evidence for mixed valence conduction in some CPs. Distinguishing between these modes of transport in OECTs could potentially overhaul how OECT active materials are designed, characterized, and tested. The field is continuously developing its description of OECT device operation and refining its understanding of polymer behavior within these devices.

1.3.2.3 **Active Materials**

In principle, any redox-active polymer that exhibits an electrochemically modulated conductivity change and/or redox conduction may be utilized as an OECT channel material. In fact, OECT-like devices have even been fabricated from non-conjugated redox polymers operating through mixed valence conduction. For OECTs based specifically utilizing π-conjugated polymers, any number of polymers with sufficient electroactivity, electrode adhesion, and conductivity modulation can be used. However, considering the bioelectronic applications of OECTs, it is often desirable to utilize active materials that are capable of electrochemical doping in physiologically relevant aqueous
electrolytes. This can present a challenge, seeing as the aliphatic side chains required for the processing and purification of common conjugated polymers are hydrophobic and therefore obstruct penetration of hydrated ions into the polymer channel and prevent full, repeated electrochemical doping in aqueous media. Thus, many common conjugated polymers (e.g. P3HT, PBTTT, and alkylated PProDOTs) are unsuitable for many of the most promising biological applications of OECTs.

Because of this challenge, PEDOT:PSS has been the first choice as an active material in OECTs and other bioelectronic devices (structure shown in Figure 1.3.4I). PEDOT:PSS is a mixture comprising doped and conducting PEDOT+ aggregates dispersed in a polyanionic PSS− matrix. PEDOT:PSS is a generally high performing material that is commercially available in large quantities as an aqueous dispersion. It has served as the active material in most of the electrophysiological applications of OECTs. However, this material brings with it some notable limitations. First, to prevent the delamination and re-dispersion of PEDOT:PSS films in aqueous electrolyte systems, crosslinking agents must be added to the film, often resulting in comprised mobility221 and greater impedance158 of the active layer. Fabricating PEDOT:PSS-based devices frequently involves the use of additives and post-treatments treatments to optimize film morphology and transport properties.222,223 Because PEDOT:PSS is a mixture often consisting of >50% PSS−, its volumetric capacitance is theoretically lower than a comparable neat conjugated polymer. Moreover, the composition of PEDOT:PSS cannot be readily characterized, and its chemical structure cannot be easily modified. So, from a materials science perspective, establishing and understanding comprehensive structural design rules for mixed-
conducting polymers using only PEDOT:PSS is not a realistic research objective. Thus, alternative active materials for aqueous OECTs are required.

Developing alternative p-type conjugated polymers for aqueous-based OECTs typically requires an electron-rich polymer backbone capable of doping within the electrochemical window of water. In the case of soluble conjugated polymers, highly polar side chains must be used to promote electrolyte uptake. Incorporation of these polar groups can be accomplished through post-polymerization modifications that convert conventional hydrophobic, aliphatic side chains with polar groups that can reduce the interfacial barriers to electrolyte uptake. These side chain de-functionalization approaches have been heavily used in the Reynolds group to develop ester-functionalized PXDOT-based materials that can be cleaved to a carboxylic acid functionality, which greatly enhances the polymer’s redox activity in aqueous media.\textsuperscript{224–226} Alternatively, the monomer precursor can be functionalized with highly polar side chains, such as oligo(ethylene oxide)-based,\textsuperscript{203,227,228} ester,\textsuperscript{229} or amide groups\textsuperscript{230} prior to polymerization. This approach, which was first demonstrated with oligo(ethylene oxide) groups by Roncali et al. in 1990,\textsuperscript{228} has since been adopted by others to develop materials for aqueous OECTs and other bio-electronic applications.\textsuperscript{194,203,227,231–234} When designing such polar-functionalized conjugated polymers, the polarity of the side chains must be carefully tuned to ensure that the material is soluble in casting solvents and can readily uptake water and ions from the electrolyte without dissolving in the electrolyte system. This can be a delicate balance; incorporation of increasingly polar and hydrophilic functionalities may promote aqueous redox compatibility but render the active material water-soluble in its doped form, resulting in delamination and precluding electrochemical characterization and device assembly.
Within the past ten years, several new conjugated polymers have been reported as OECT active materials. Because this thesis primarily focuses on PT- and PXDOT-based conjugated polymers, a non-exhaustive summary of such active materials is shown in Figure 1.3.4. It should be noted that the particular OECT materials presented in this thesis are excluded from this listing and will be described and discussed in later chapters. For a comprehensive overview of the various conjugated polymers that have been used in aqueous OECTs, the reader is directed to several recent manuscripts and reviews.\textsuperscript{201,235–237}

Figure 1.3.4 – Structures of common PT- and PXDOT-based aqueous OECT active materials reported in the literature. Black structures represent polymer backbone. Blue structures represent standard polar. Red structures represent ionic side chains.
1.4 Dissertation Thesis

This thesis explores several concepts relating to the formulation, structural modification, and characterization of π-conjugated polymers used in both electrochromic devices and electrochemical transistors. The materials studied in this work chiefly incorporate dioxythiophene-based backbones that feature structurally diverse comonomers as well as solubilizing and/or functional side chains. Focusing on the optical and electrochemical properties of conjugated polymer, this thesis presents approaches towards the design of polymeric active layers targeted redox applications.

CHAPTER 2 will introduce and outline the various experimental methods utilized in this thesis and discuss the interpretation of these measurements.

Next, CHAPTER 3 will describe an approach toward developing solution-processable, high-contrast, black-to-transmissive materials for electrochromic devices using color-mixing of PProDOT-based ECPs. This chapter will outline the challenges associated with developing black polymeric electrochromes and demonstrate how various PProDOT-based electrochromic polymers can be combined to develop stable and color-neutral electrochromic films with minimal intermediate coloration.

The work presented in CHAPTER 4 will investigate the structural effects governing the properties and performance of aqueous-compatible polythiophenes for application in OECTs. This chapter will evaluate the effect of the length of the substituent glycol side chain on the microstructure, capacitance, and aqueous electrochemistry of this popular class of polymers.
Following this work, CHAPTER 5 will motivate the development of PProDOT-based OECT active materials as an alternative to traditional polythiophenes. Through these studies, the design criteria for polar-functionalized polythiophenes and PProDOTs will be discussed and compared, underscoring important differences between these seemingly similar classes of conjugated polymers.

Finally, CHAPTER 6 will introduce in situ neutron reflectivity as a novel technique for studying the volumetric and interfacial changes that occur in two polymers upon electrochemical doping processes in aqueous media. These studies will showcase the effects of polymer functionalization and side chain density on redox properties, microstructure, and swelling behavior of aqueous-compatible PProDOTs. Notably, this work utilizes a novel application of neutron reflectivity as an in situ characterization technique for studying potential-dependent physical changes associated with the electrochemical doping reaction, thereby highlighting a greater need for understanding interfacial processes in redox-active conjugated polymers.
CHAPTER 2. EXPERIMENTAL METHODS

Contributions were made to this work by several collaborators at the Georgia Institute of Technology (GT), Oak Ridge National Laboratory (ORNL), Imperial College London (ICL), Northwestern University (NU), and BASF. Dr. Dylan Christiansen (GT) was responsible for the conception, synthesis, and structural characterization of a polymer presented in CHAPTER 3. Michael Kuepfert (BASF), Joe Babiarz (BASF), and Dr. Kin Lo (GT) were responsible for the synthesis of other polymers presented in CHAPTER 3. Dr. James Ponder (ICL/GT) and Maximilian Moser (ICL) were involved in the synthesis and structural characterization of the polythiophene family detailed in CHAPTER 4. Dr. James Ponder (ICL/GT) and Brandon DiTullio (GT) performed the synthesis and structural characterization of the polymer series presented in CHAPTER 5 and CHAPTER 6. The planar OECT measurements reported in CHAPTER 5 were performed by Dr. Jonathan Rivnay and Katrina Barth (NU). The neutron reflectivity experiments in CHAPTER 6 were accomplished through a collaboration with Dr. Zach Seibers (GT) and Dr. Jim Browning (ORNL), who greatly assisted in the planning, execution, and interpretation of this work and the development of the reflectivity models. Working and counter electrodes for these experiments were fabricated by Dale Hensley (ORNL). Richard Bedell (GT) is gratefully acknowledged for his contributions to developing the OECT platform presented in CHAPTER 2.6.2.

This chapter outlines the various experimental techniques used to generate the results presented in this thesis. Largely, these methods include various optical and electrochemical analyses of conjugated polymer films. Considerations for solution-based
processing techniques of conjugated polymer films are also discussed. The content in this chapter will surround the importance of these measurements as well as considerations for proper execution. Experimental details not explicitly outlined here in CHAPTER 2 will be expanded upon in the respective dissertation chapters through additional descriptions and/or referral to relevant literature.

2.1 Materials and Structural Characterization

All materials, reagents, substrates, and electrodes used to synthesize and characterize the polymers in this thesis were procured from commercial suppliers and used as obtained, unless otherwise noted. Tin-doped indium oxide (ITO) glass electrodes were purchased from Delta Technologies (sheet resistance of 8–12 Ω sq⁻¹, 7 mm × 50 mm × 0.7 mm). Platinum interdigitated electrodes were obtained from MicruX Technologies, with electrode specifications described in CHAPTER 2.6.2. Planar OECT electrodes were prepared and provided by Dr. Jonathan Rivnay (NU). Substrates for neutron reflectivity were obtained and prepared by Dr. Jim Browning and Dale Hensley (ORNL), as described in more detail in CHAPTER 2.2.2.5. Commercial single-junction Ag/AgCl reference electrodes (3 M NaCl/H₂O inner solution) were purchased from BASi Scientific and used for most aqueous electrochemistry presented in this dissertation. A capillary-sized single-junction Ag/AgCl reference electrode (3 M KCl/H₂O inner solution), used exclusively for in situ neutron reflectivity measurements, was purchased from MIROM Medical & Research Equipment, Ltd.

For preparation of organic electrolytes, propylene carbonate (PC, Acros organics, 99.5 %, purified using a solvent purification system) was used as the electrolyte solvent.
Tetrabutylammonium hexafluorophosphate (TBAPF₆, Acros Organics, 98%, purified by recrystallization from hot ethanol) was dissolved in the PC at RT, yielding an electrolyte concentration of 0.5 M. For aqueous electrochemistry, ultrapure water (solution resistivity $> 18.2 \ \text{M}\Omega\cdot\text{cm}$) was obtained from an in-house water purification apparatus and used to prepare aqueous electrolyte solutions. Aqueous electrolyte salts included phosphate buffered saline powder (1×PBS, pH = 7.4, Sigma Aldrich) and sodium chloride (NaCl, biotechnology grade, Amresco). Unless otherwise noted, all electrolytes were degassed with argon for at least ten minutes prior to use.

2.1.1 Approaches to Synthetic Collaboration

As described previously, the conjugated polymers studied in this thesis were prepared by several academic collaborators and industrial partners. The polymerization techniques utilized to prepare these materials utilize either Stille cross-coupling polymerization or direct (hetero)arylation polymerization (DHAP). Both of these polymerization techniques are Pd-catalyzed C-C bond forming reactions which join aromatic repeat units. In the case of the PTs and PXDOTs studied in this thesis, the bond formation occurs at the α position of the thiophene ring.

Stille cross-coupling involves the reaction of organotin and halogenated (usually brominated) starting materials to form C-C $\sigma$ bonds. For a thorough discussion of Stille cross coupling as applied to π-conjugated materials, the reader is directed to the theses of Dr. Rylan Wolfe$^{239}$ and Dr. Chi Kin Lo.$^{71}$

DHAP involves Pd-mediated C-H activation to join a halogenated (usually brominated) arene with an unmodified arene. The use of bifunctional arenes in these cross-
coupling reactions enables polymerizations yielding \( \pi \)-conjugated macromolecules. The theses of Dr. James Ponder\(^{72} \) and Dr. Justin Kerszulis\(^{74} \) provide excellent discussions and examples of DHAP, especially for preparing PXDOTs.

The electrochromic materials studied in CHAPTER 3 were synthesized using both Stille cross-coupling polymerization and DHAP, depending on the polymer. The glycol-functionalized PTs reported in CHAPTER 3 were synthesized using Stille cross-coupling polymerization. All of the PProDOTs reported in CHAPTER 4 and 5 were prepared by DHAP. The particular synthetic details for each material, which will be indicated in the respective dissertation chapters, may be found in the APPENDIX and/or the indicated literature.

2.1.2 Structural Characterization

The structural characterization for the polymers studied in this thesis can either be found in referenced literature or in the supporting APPENDIX, as indicated in the respective thesis chapters. \(^1\)H NMR and/or \(^13\)C NMR spectra for monomers, molecular precursors, and polymers (when necessary) were acquired on a Varian Mercury Vx 300 MHz instrument using CDCl\(_3\) as the solvent, unless otherwise indicated. The residual CHCl\(_3\) peak was used as a reference for all reported chemical shifts (\(^1\)H: \( \delta = 7.26 \) ppm, \(^13\)C: \( \delta = 77.16 \) ppm). Unless otherwise specified, most gel permeation chromatography (GPC) was performed using a chloroform Tosoh EcoSEC GPC instrument with a refractive index detector to determine the number average molecular weight (\( M_n \)), weight average molecular weight (\( M_w \)), and dispersity (\( \bar{D} \)) relative to polystyrene (PS) standards. GPC was performed in a CHCl\(_3\) solvent at 40 °C. Elemental analyses were conducted by Atlantic
Microlab, Inc. (Norcross, GA). All characterization was performed to ensure adequate compositional and structural purity prior to any further measurements, unless otherwise noted.

2.2 Solution Processing onto Substrates and Electrodes

Among the many attractive properties of π-conjugated polymers is their ability to be processed using facile, solution-based techniques without the need for extreme temperatures, pressures, or controlled environments. While the planarity and rigidity of π-conjugated systems usually makes dissolution of these materials difficult, functionalization of the conjugated backbone with flexible side groups can promote solubility of these materials in many common processing solvents, enabling full purification and structural characterization by spectroscopic and chromatographic techniques. If sufficiently soluble, π-conjugated materials can also be formulated into solutions with appropriate viscosity for many industrial coating techniques, allowing for the serial patterning and printing of optoelectronic device components. The most effective solubilizing groups exhibit a high degree of conformational freedom, such as branched aliphatic groups, which promote solubility in organic solvents. Polar functionalities, like esters and ionic groups, may also be installed to impart solubility in polar organic or even aqueous solvents.

Most of the results presented in this thesis were obtained from samples coated from solutions onto planar substrates to form thin, solid films. A range of solution-based processing techniques were used, as outlined below. Each of these coating techniques involve constraints relating to solvent vapor pressure, solution viscosity, and substrate orientation. Depending on the desired film homogeneity, spatial resolution, or processing
speed, one coating technique may be chosen over another. Frequently, some degree of optimization was required to achieve the desired film quality and thickness.

This section details the preparation and processing of conjugated polymer solutions on planar substrates, primarily for the purpose of optical, electrochemical, and microstructural characterization. Considerations for effective processing are outlined.

### 2.2.1 Solution Preparation

Polymers were obtained as dry solids after synthesis, purification, and isolation. Depending on the molecular weight, polymer structure, and isolation method, these solids can adopt a range of topologies and appear as fine powders, crumbs, fibers, flakes, or a solid bolus. The solids can be dissolved in various solvents, depending on the required final solution concentration, viscosity, temperature, and vapor pressure. In the work presented in this thesis, polymers were dissolved in toluene, chloroform, or a chloroform/chlorobenzene mixture for processing. Dissolution was accomplished by stirring the polymer in the solution in a vial with a magnetic stir bar for a period of time ranging from 1 h to several days, depending on the solubility of the material. In many cases, the concentration of the solution is an important known parameter for ensuring coating reproducibility and normalizing measurements. Accordingly, it is important for the lids of vials to be secured with some sort of tape (e.g. Parafilm, Teflon tape) to minimize solvent evaporation during dissolution and storage.

For materials with extremely low ionization energies (IEs), such as the PXDOTs described in CHAPTER 5, aged solutions can undergo partial doping and simultaneous aggregation while in solution. Ambient doping of polymer solutions may be caused by
environmental oxygen or by the progressive acidification of chloroform-based solutions. For the studies conducted in this thesis, processing from aged, partially doped, or aggregated solutions did not seem to significantly impact the final optical or electrochemical properties of the polymer films once conditioned. However, to minimize the possibility of any potential pH-related degradation, few chloroform-based solutions were used beyond one month following initial formulation.

2.2.2 Substrate Preparation

The surface energy, roughness, and cleanliness of substrates can be incredibly important for determining the wetting properties of the polymer solution, the film formation process, and the microstructure of the resulting polymer film. The effects of surface functionalization on film formation were not a scientific focus of this thesis. Rather, substrates underwent basic cleaning procedures to remove any surface contamination and/or adventitious carbon that could modify the integrity of the polymer-substrate interface or compromise electrochemical measurements. For a more detailed overview of treating and cleaning electrode materials, the reader is directed to the cited literature.240

Considering that the organic processing solvents were relatively low surface energy, sufficient wetting was achieved when coating solutions onto the high-energy native oxide layers on silicon, glass, and indium tin oxide (ITO) substrates. Moreover, the particular combination of coating techniques and solvents used in this work promoted rather rapid drying times (< 2 s), thereby minimizing any possibility of solution de-wetting after coating. Surface modifications techniques were only used if required to promote adhesion during electrochemical conditioning.
2.2.2.1 Basic Cleaning of Substrates and Electrodes

All planar substrates (glass, silicon) and electrodes (ITO/glass, Pt interdigitated electrodes) were cleaned by first rinsing with distilled water and sonicating in a series of separate cleaning solutions for at least 5 min each. The cleaning solutions used included sodium dodecyl sulfate dissolved in distilled water, neat distilled water, acetone, and isopropanol. Clean and unused ITO/glass substrates were stored in isopropanol prior to use. Before coating, the substrates were gently rinsed with clean isopropanol and dried under a gentle argon stream to prevent residue formation. Where indicated, some substrates were further cleaned by treatment in a UV-O₃ chamber. Unless otherwise stated, this cleansing procedure was typically sufficient for the optical and electrochemical characterizations described later.

2.2.2.2 Surface Modification with Alkyl Phosphonic Acids

Modification of ITO/electrode surfaces with hydrophobic surface treatments can be a strategy for improving the interfacial adhesion between the polymer and electrodes. While most studies in this thesis required no such modification of the electrode surface, one polymer in CHAPTER 3 showed a propensity of delaminate from electrodes when electrochemically cycled in organic electrolytes. Accordingly, ITO/electrodes were modified by treatment with an alkyl phosphonic acid prior to coating. The phosphonic acid group is thought to covalently anchor to the oxide surface of the electrode, while the hydrophobic tail orients away from the substrate, yielding a so-called self-assembled monolayer. The monolayer of alkyl tails lowers the surface energy of the electrode, thereby reducing the interfacial tension between the polymer and electrode and promoting
the adhesion of the polymer to the electrode during electrochemical cycling. This approach has been demonstrated in a recent study by Pittelli et al. that focused on interfacial modification of ITO specifically for polymer-based electrochromic devices.\textsuperscript{127}

To prepare ITO/glass electrodes for SAM modification, they were first cleaned by basic solution sonication techniques outlined above. Then, the electrodes were dried under an argon stream and cleaned in a UV-O\textsubscript{3} chamber for 20 min, with the conducting ITO side facing up. The purpose of this treatment was to remove any organic contaminants and adventitious carbon from the surface, generating the highest surface population of oxide groups to participate in reaction with the phosphonic acid group. After UV-O\textsubscript{3} treatment, a solution of \textit{n}-hexyl phosphonic acid (10 mM in ethanol) was carefully dropped onto the surface of the electrode until the solution had begun to bulge due to surface tension. The solution was left on the electrode undisturbed for 15 minutes and then gently rinsed with isopropanol.

2.2.2.3 **Piranha Cleaning Methods**

For preparation of samples for GIWAXS analysis, more thorough cleaning protocol must be employed to remove any surface contamination that could result in stray scattering or inadvertent sample-to-sample variations. Planar Si substrates were subjected to the same solution cleaning protocol described in CHAPTER 2.2.2.1, stored in a bottle of distilled water, then later cleaned using acidic piranha etch. Piranha is a strong acid and oxidizing agent that removes all organic contaminants from the substrate, leaving only the native SiO\textsubscript{x} layer on the substrate. Given the highly acidic and reactive nature of piranha, full personal protective equipment (glasses, gloves, long pants, and lab coats) and safety
equipment (ventilated hood, sash, acid spill kit, eye wash) should be employed and available when working with this substance.

Piranha etch was prepared in a clean 500 mL glass beaker (no visible cracks) in a ventilated fume hood. First, 72 mL of concentrated sulfuric acid (H₂SO₄) was added to the beaker with a clean glass graduated cylinder. Once the temperature stabilized, a separate clean, glass graduated cylinder was used to slowly and carefully add 24 mL of hydrogen peroxide (H₂O₂) by pouring along the inner wall of the beaker. This mixture yields a 3:1 v/v solution of H₂SO₄/H₂O₂, which should begin reacting and bubbling immediately, indicating the formation of the super acid needed for cleaning. The ratio of these two components should never exceed 3:1, as the solution may become highly unstable. Once reacting, the beaker was transfer to a hot-plate pre-heated to approximately 70 °C to maintain the reactivity of the solution. The temperature of the hot plate was monitored at a distance using an IR thermometer.

Using clean stainless-steel tongs, the Si substrates were removed from the bottle of distilled water and gently placed at the bottom of the active piranha solution. Cleaning of the substrates is associated with rapid bubbling and heat generation. Once the substrates were immersed in the solution for approximately 20 min, they were gently removed with tongs, rinsed using a strong stream of distilled water, and stored in a new clean bottle of distilled water. Upon rinsing, the distilled water should wet the surface of the substrate completely and uniformly. If any beading or de-wetting is observed, the substrate has not yet been properly cleaned and needs to be returned to the piranha etch. Used piranha should be allowed to cool and decompose in a fume hood and then be properly disposed as acid waste.
The Si substrates can be stored in a jar of clean distilled water for up to a week, if covered. Immediately prior to coating, substrates were removed with clean tweezers, touching only the outer corner, and dried under a stream of argon gas.

2.2.2.4 Electrode Polishing

For electroanalytical studies performed on button electrodes, the electrode substrate must be polished prior to depositing the polymer on the electrode. Polishing the electrode reduces the roughness of the surface, leading to a well-defined electrode surface area. This practice should be performed prior to every measurement to also remove any adsorbed contamination from previous measurements. When using glassy carbon (GC) electrodes, polishing is especially important for increasing the “activity” of the electrode.\textsuperscript{240} Polishing is performed by gently wiping the electrode on a felt polishing pad coated in an alumina-water slurry in varied “figure 8” motions, periodically rotating the polishing pad 90 °. In this work, polishing was performed using pastes of alumina and water with successively smaller particle sizes (3 μm, 1 μm, and 0.05 μm), followed by thoroughly rinsing the electrode with distilled water. A properly polished GC electrode should appear smooth and mirror-like with no scratches, dull regions, or blemishes (excluding those in one’s own reflection).

2.2.2.5 Substrates for Neutron Reflectivity

Substrates for neutron reflectivity studies (CHAPTER 6) were prepared and provided by Dr. Jim Browning and Dale Hensley at ORNL. Round monocrystalline Si substrates (diameter = 51 mm, thickness = 1 cm) were first cleaned by immersion into piranha acid etch for 20 min, followed by rinsing with copious amounts of DI H\textsubscript{2}O, and
finally dried using filtered N\textsubscript{2}. Cleanliness was confirmed by ellipsometry before transferring to a N\textsubscript{2} glove box for electrode deposition. The clean substrates were coated with a thin chromium adhesion layer (thickness \( \approx 4 \) Å) following by a gold electrode layer (thickness \( \approx 30 \) Å) by colleagues at the Center for Nanomaterials Science at ORNL. These substrates were measured by X-ray reflectivity at ORNL to confirm film electrode thickness and uniformity. The Au-coated Si substrates were used as the WE in the experiment. The CEs were fabricated using a similar process to apply a rough 30 nm Pt layer directly onto an identical monocrystalline Si wafer.

Prior to coating with a polymer solution, the Au-coated Si substrates were cleaned with a series of solvents (chloroform (if needed), DI water, acetone, and isopropyl alcohol). Next, the substrates were dried under filtered N\textsubscript{2} and thoroughly cleaned in a UV-O\textsubscript{3} chamber for 15 minutes.

2.2.3 Drop Casting

Drop-casting films from solution is a straightforward way to deposit polymer films on planar substrates. This technique can be performed by pipetting a known volume of a polymer solution directly onto a substrate and allowing to solution to dry in the ambient environment. In this work, drop-casting is used to deposit polymer films onto the active area of a button electrode and used for electroanalysis.

When using a polymer solution of a known concentration, the final mass of the polymer film can, in principle, be determined. This allows for normalization of current, redox capacity, and other properties to the mass of the active polymer film. However, when drop-casting from low-boiling solvents (e.g. chloroform), one should make efforts to
minimize the amount of polymer that is inadvertently left in the dispensing tip of the pipette from solvent evaporation. This can introduce errors into mass normalization, which is particularly important for studies concerning electrochemical supercapacitors, where mass capacitance is a critical figure-of-merit.

While drop-casting is a straightforward and quick way to deposit films, it has several important limitations that make its usage for electroanalysis somewhat questionable. First, drop-cast films are usually quite heterogeneous in thickness across the width of the film due to non-uniform drying associated with Marangoni flow (i.e. so-called “coffee staining” effects). Accordingly, while it can be easy to calculate the approximate mass of the polymer film deposited, extracting a precise thickness is rather difficult. Therefore, electroanalytical calculations requiring a known and relatively uniform thickness may lead to erroneous results (e.g. determination of ion diffusion coefficient by chronocoulometry or ionic conductivity/diffusion coefficient by electrochemical impedance spectroscopy). Moreover, the heterogeneity caused by drop-casting can drastically affect the uniformity and the nature of charging and of mass transport processes. Such heterogeneity (especially sample-to-sample variations in heterogeneity) can obfuscate results of electrochemical impedance spectroscopy (EIS), which is highly sensitive to non-uniform charging.

Another important drawback relating to drop-casting relates to the practical challenge of drop casting active material only the active area of the button electrode, which is often quite small (area, \(a < 0.1 \text{ cm}^2\)). Drop-cast solutions comprising low surface energy solvents (e.g. chloroform) tend to spread over large areas, depositing polymer mass outside of the active area of the electrode. Depending on the conductivity of the polymer in the
doped state, the excess polymer outside of the active electrode area may or not be accessed electrochemically, which again can cause errors in purported mass-normalized measurements. Furthermore, the presence of excess polymer outside of the electrode active area causes rather distinct changes in the overall shape of the resulting cyclic voltammogram. This observation will be expanded upon in CHAPTER 2.3.1.

2.2.4 Spray Coating

Like drop casting, spray coating is a straightforward and facile method for fabricating thin films. Spray-coating is particularly advantageous when coating large surface areas. This technique involves the atomization of a solution into small droplets, which are ejected from a nozzle under the pressure of a carrier gas and deposited onto an underlying substrate. Typically, a solvent with high vapor pressure and low viscosity is selected so that the droplets dry quickly upon deposition on the substrate. Because of this fast-drying process, there is little opportunity for solution droplets to pool, migrate, and/or de-wet once they encounter the substrate. For the same reason, the microstructure of the resulting polymer film is usually disordered and/or isotropic, as the chains are in a kinetically trapped conformation almost immediately upon deposition and cannot slowly coalesce, order, and potentially crystallize upon film solidification as they may with other solution-based methods. Another unique consequence of this rapid drying process is that spray coating can be a buildable technique; that is, additional material can be cast on top of an existing film without the re-dissolution or disruption of the underlying layer.

Spray coating usually results in extremely rough thin films \( R_q \approx 25–50\% \) of total film thickness), but because this roughness persists on short length-scales (nm–μm range),
properly spray cast conjugated polymers seem homogeneous to the eye. They can, however, exhibit at high degree high diffuse scattering, resulting in a hazy or matte appearance.

To generate results in this thesis, spray coating was performed using 2–5 mg mL⁻¹ polymer solutions in chloroform or toluene. Solutions were loaded into an Iwata-Eclipse HP-BC airbrush and sprayed at room temperature, unless otherwise noted, using an argon carrier gas (10–40 psi). For the films studied in 0, films were maximum transmittance (%T) of 10% ± 2%, as monitored at the wavelength of maximum absorbance (λ_max) for the dedoped film.

2.2.5 Blade Coating

Blade coating is a meniscus-guided coating technique in which a planar coating head (i.e. the “blade”) is using to pull the meniscus of the coating solution across a substrate. Depending on the angle and velocity of the blade, the solution viscosity and concentration, the solution loading volume, the coating temperature, and the gap height, a range of film thicknesses and microstructures can be achieved. Accordingly, blade coating can require extensive parameter optimization to achieve the desired film quality. Blade coating (much like drop casting) allows for longer solidification time and, depending on the properties of the coating solvent, can produce heterogeneous films due to gradients in surface tension, temperature, and capillary flow as solvent evaporates. However, blade-coated films are generally more uniform and smoother than drop-cast films, and any heterogeneity in thickness of roughness is usually confined to the outer edges of the film. Because blade coating involves a directional shear of the coating solution, this technique
can also be used to induce anisotropy in resulting film. For more detailed physical descriptions of the utility of blade coating and other meniscus-guided techniques in organic electronics, the reader is directed to cited literature.\textsuperscript{242}

Blade coating reported in this work was performed using a custom-build blade coater equipped with a clean glass blade. Typical polymer solutions were mixed to a concentration of 10–25 mg mL\textsuperscript{-1} of polymer in an organic solvent, such as chloroform, chlorobenzene, or toluene. Solution volumes ranging from 5–25 μL were loaded under the blade (100–200 μm gap height) and coated at blade speeds ranging from 1–4 mm s\textsuperscript{-1}. Depending on the coating properties of the given solution, the coating temperature was tuned to promote solidification and ensure consistent film quality. After the films dried, cotton swabs were used to remove the irregular edges of the film, leaving a rectangular and visually homogeneous final film.

2.2.6 Spin Coating

Spin coating is perhaps the most popular solution-based coating techniques used for studying conjugated polymers. This method involves depositing a solution evenly across a flat substrate, which rotates at high speeds (≥ 1000 rpm). During rotation of the substrate, the solution experiences increased airflow and radial shearing. In the initial stages of coating, excess solution is expelled, leaving a thin and uniform layer of solution on the substrate. Further rotation involves additional thinning of this solution layer followed by solvent evaporation and film solidification, beginning at the center of the substrate and rapidly progressing outward. The thickness of the final film can be tuned by changing the solvent properties, solution concentration/viscosity, and spin speed.
If done properly, spin coating yields uniform thin films with nanometer-scale (or lower) roughness. Once the coating parameters are optimized, this spin coating is exceptionally reproducible. Film formation is predominantly dictated by fundamental fluid physics and has fewer user-controlled variables than blade coating, allowing for the widespread adoption of this technique, especially in the semiconductor industry. One notable drawback of spin coating is the large amount of material lost during the coating process. In fact, only approximately 2–5% of material deposited onto the substrate is thought to end up in the final film, while the rest of the active material is flung off the substrate and discarded. Therefore, spin coating is undesirable for fabricating films of valuable materials of limited supply, such as many of polymers presented in this thesis.

In this work, spin coating is used only to fabricate samples for neutron reflectivity studies—a unique setting where large, highly uniform, and smooth films are critical for extracting information about interfacial phenomena. These studies, which are further detailed in CHAPTER 6, utilized Au-coated Si wafers as substrates. These substrates were obtained and prepared by colleagues at Oak Ridge National Laboratory, as described in CHAPTER 2.2.2.5. The polymer coating solution (10–20 mg mL\(^{-1}\) in chloroform) was filtered through a 0.20 μm Teflon syringe filter using a glass syringe, which removed any insoluble particles that would otherwise compromise film uniformity and homogeneity. For spin coating, 1.5–2 mL the desired polymer solution was deposited onto the clean Au-coated Si wafers via syringe and spun at RT on a ventilated spin coater. The coated was performed at 1000 rpm (acceleration = 1000 rpm s\(^{-1}\)) for 30 s. This coating procedure yielded homogeneous pink films with an exceptional mirror-like finish, suggesting low surface roughness.
2.3 Electrochemical Characterization

The electrochemical characterization of conjugated polymers is a central component of this thesis. The fundamental working mechanism of both ECDs and OECTs involves electrochemical redox processes in which the oxidation state of the active conjugated polymer film is repeatedly modulated and subject to electrolyte flux. The various electroanalytical techniques described in this section provide important information about the electrochemical properties, charging behavior, capacitance, and stability of the many polymers presented in this work. For all electroanalyses, the polymers of interest were evaluated as thin solid films cast from solution directly onto an electrode, as their utility in electrochemical devices usually involves the polymer as a solid active layer. To develop a more complete understanding of analytical electrochemistry, especially for studying electroactive polymers, the reader is directed to several key textbooks\textsuperscript{185,244,245} and papers.\textsuperscript{57,246}

2.3.1 Cyclic Voltammetry

Cyclic voltammetry (CV) provides a wealth of information about the nature of electron transfer processes and is applicable to a broad range of materials. When applied to redox-active $\pi$-conjugated polymers, CV can either be used both as a means for synthesizing conjugated polymers (via electropolymerization) as well as a tool for characterizing their redox behavior. Because all of the materials studied in this thesis were synthesized using chemical (as opposed to electrochemical) means, CV was utilized as an analytical method for probing the oxidation/reduction onset, charge storage capacity, and redox stability of the polymers of interest.
Like most electroanalytical techniques, CV is performed using a three-electrode cell comprising a working electrode (WE), a counter electrode, (CE) and a reference electrode (RE)—all of which are connected to a potentiated and immersed in an electrolyte. In the standard three-electrode set-ups, the WE is the site of the electron transfer process under study. The potential of the working electrode is precisely controlled, and its current is monitored. During CV experiments, a triangular potential waveform is applied to the WE. The potential of the WE is swept at a constant rate relative to a high-impedance RE. The RE consists of a redox couple with a known, stable equilibrium potential. Because the RE does not theoretically pass any current throughout the duration of the experiment, its potential remains relatively constant. Therefore, redox processes observed can be related to a known electrochemical potential. The RE and WE should be placed close together to minimize the potential drop (also called “i-R drop”) in the cell. Current generated at the WE flows to/from CE, which completes the electronic circuit in the cell. The potential of the CE is adjusted by the potentiostat such that the total charge passed at the CE and WE are equivalent. To ensure that the potential of the CE does not limit the redox process, large CE (with areas at least double that of the WE) are typically used to ensure that comparable current can be passed without exceedingly large potentials. When studying redox processes at the WE, inert CE materials should be chosen. This ensures that charge compensation is accomplished through capacitive charging only and not by any faradaic process that could change the electrolyte chemistry.

A detailed schematic of the three-electrode configuration used in this work is provided in Figure 2.3.1. Both aqueous and organic electrolytes were employed, depending on the target application of the polymer. Prior to electroanalysis, the electrolytes were
degassed with argon and kept under an argon blanket throughout the duration of the study, unless otherwise noted. Degassing was performed to exclude confounding effects of oxygen on the current response and stability of the materials. The CV traces reported in this thesis were recorded using an EG&G Princeton Applied Research 273A potentiostat/galvanostat (with CorrWare software), a Reference 3000 Gamry potentiostat/galvanostat/ZRA (with Gamry Framework 6.5 software), a Pine AFCBP1 bipotentiostat (with Aftermath Software), a Pine WaveNow potentiostat (with Aftermath software), and a Bio-Logic VSP (with EC-Lab software). For the work presented in this thesis, both planar electrodes (e.g. ITO/glass) and button electrodes (e.g. GC) were used as working electrodes. These electrodes were directly coated with a thin film of the polymer under study, as described in CHAPTER 2.2, allowing for the direct characterization of the redox response of each material. Details for the casting of specific materials will be given in the respective dissertation chapters.

Figure 2.3.1 – Schematic showing prototypical three-electrode cell used for standard voltammetry measurement, as applied to the work conducted in this thesis. Identifying labels are in bold with example material(s) shown beneath.
Depending on the electrolyte system used, two unique silver-based REs were employed. For electrochemistry conducted in aqueous electrolytes (e.g. sodium chloride in water, NaCl/H₂O), a commercial single-junction Ag/AgCl RE was employed. The Ag/AgCl RE of a chloridized Ag wire immersed in a 3 M aqueous KCl solution, which was encased in a glass tube and sealed with a porous frit allowing for contact with the electrolyte. For most ambient conditions, this electrode corresponds to a half wave potential E₁/₂ ≈ +0.21 V vs. the normal hydrogen electrode (NHE). Precluding a detrimental user error, the equilibrium of such commercial electrodes tends to be stable over time. If needed, calibration can be performed using the ferrocyanide/ferricyanide redox couple. For electroanalysis performed in organic electrolytes, a single-junction Ag/Ag⁺ pseudo RE was used. This electrode consists of a polished Ag wire immersed in a solution of silver nitrate (AgNO₃, 0.010 M) and tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.5 M) in acetonitrile (ACN). Because this Ag/Ag⁺ redox couple can drift, this RE was routinely calibrated against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple, whose half-wave potential (E₁/₂) lies around +0.6 – +0.7 V vs. NHE when studied in dilute CAN solutions at room temperature. Calibration of the Ag/Ag⁺ electrodes used in this work typically resulted in an E₁/₂ values for Fc/Fc⁺ ranging from +0.025 – +0.100 V vs. Ag/Ag⁺. Indicating the identity and equilibrium potential of the RE is necessary when reporting electroanalytical data.

Inert materials (e.g. GC, Pt) were used as CEs. Special considerations are required when using Pt CEs in aqueous electrolytes. The high exchange current density for hydrogen evolution on the Pt surface increases the likelihood of side reactions with the aqueous electrolyte, especially under conditions with high WE current and relatively small CE area.
From the profiles of the triangular WE voltage sweep and current transient, a CV showing current as a function of voltage is obtained. An example of such data is given in Figure 2.3.2, which shows the CV of a PProDOT polymer film spray cast on an ITO/glass electrode and cycled in a 0.5 M TBAPF₆/PC electrolyte. The voltage sweep in Figure 2.3.2A corresponds to a scan rate of \( v = \frac{dV}{dt} = 50 \text{ mV s}^{-1} \), scanning between -0.8 V to +0.8 vs. Ag/Ag⁺. The first half of the sweep begins in the anodic direction, resulting in positive current transients from polymer oxidation (p-doping). The second half of the sweep in cathodic direction is associated with negative currents representing the discharging of the polymer to its initial neutral (de-doped) state. Superposition of the current and voltage parameters yields the CV profile shown in Figure 2.3.2B.

![Figure 2.3.2](image)

**Figure 2.3.2** – A) Exemplary triangular voltage waveform and current response recorded for a cyclic voltammogram of a PProDOT film in a 0.5 M TBAPF₆/PC electrolyte. Dashed lines denote the slope of the potential sweep, corresponds to the scan rate, \( v \). B) Cyclic voltammogram constructed from the data in panel A, with shaded area and selected points. Arrow indicates the initial anodic direction of the sweep. Potential is reported vs. Ag/Ag⁺ (Fc/Fc⁺ \( E_{1/2} = +0.52 \text{ mV} \)).
Typically, the first 1–10 CV cycles of a conjugated polymer look different than the rest. For this reason, 10–20 CV cycles are performed on the as-cast pristine films of conjugated polymer films before obtaining repeatable, reportable CV data. During this time, the CP film undergoes rearrangement as chains are repeatedly doped/de-doped. This phenomenon, which has been identified repeatedly in the literature for a range of conjugated polymers, has been referred to as “electrochemical conditioning,” “electrochemical annealing,” “a break-in process,” and/or “a memory effect,” depending on the source.\textsuperscript{57,129,248–253} It is thought that this electrochemical conditioning effect is the result of a rearrangement of pristine films (which are usually in some kinetically trapped disordered structure) into ordered structures with enhanced chain planarity and intermolecular aggregation as required to stabilize charge carriers. These hypotheses are supported by the overall red-shifting of the neutral $\pi-\pi^*$ absorbance and the overall lowering of the redox potential that occurs after conditioning for many materials.\textsuperscript{104,129} The break-in effect is also associated with incorporation of ions and solvent into the polymer matrix.\textsuperscript{251,254} The exact nature of this conditioning is likely dependent on the particular polymer structure, film preparation method, and the polymer-electrolyte compatibility. In this thesis, the reported CVs represent those obtained after several full doping/de-doping cycles until overlapping i-V characteristics were obtained, indicating the material had reached steady-state behavior.

The cyclic voltammograms of conjugated polymer films are complex and differ significantly from typical CVs of idealized, one-electron redox couples, thereby preventing classical descriptions of voltammetric symmetry and reversibility. Nonetheless, CVs of conjugated polymers, such as that presented in Figure 2.3.2B, can be analyzed to obtain a
useful information about the polymer in question. Between -0.8 and -0.5 V, little current is passed as the polymer is in its de-doped form and not undergoing any notable redox process. The little current in this region arises from capacitive charging of the underlying electrode. Scanning anodically to $p1$, a sharp rise in positive current is associated with the principal onset of oxidation of (E$_{ox}$) of the polymer. While E$_{ox}$ (or E$_{red}$, in the case of n-type polymers) is commonly used to determine the HOMO (or LUMO), and therefore the IE (or EA) of a material, it is important to note that redox potentials also depend on the interfacial thermodynamics and kinetics associated with electrolyte uptake and electron transfer. Therefore, the practice of deriving intrinsic energy levels from electrochemical data, though widespread, is a bit of a shortcut that subject to error from extrinsic sources.

After $p1$ in Figure 2.3.2B, the current corresponding to this oxidation wave reaches a local maximum at $p2$, then climbs to another oxidation wave at $p3$ at approximately 0.0 V. Following the second oxidation wave at $p3$, the current drops and reaches another subtle peak at $p4$, then plateauing around $p5$. Discharging the polymer yields a similar cathodic plateau until $p6$, where the polymer begins to return to its initial state.

The origin of these redox peaks and capacitive plateau is an area of great interest in the electroactive polymer community. It has been hypothesized that different redox peaks may be attributed to the heterogeneous energetic landscape of the polymer film, where domains with different extents of inter- and intra-molecular coupling give rise to electrochemically resolvable populations of chromophores with different extents of order.$^{255-257}$ The cause of such capacitive-like plateaus in conjugated polymer CVs is debated in the field; it has been attributed to a range of phenomena, depending on the system under investigation. Various interpretations have ascribed these capacitive-like
charging of CPs after doping to the presence of interacting and overlapping discrete redox processes, capacitive charging of internal interfaces, reorganization of the ion distribution within the film, and/or a combination of these effects.

Integration of the CV characteristics, as shown via the gray shade in Figure 2.3.2B, yields the product of the gross charge stored \( Q \) and the scan rate \( v \). Thus, the total charge passed during the individual charging (or discharging) can be determined by integration of the anodic (or cathodic) portions of the CV. This is demonstrated below in Equation 2, which shows the expression of the basic definition of charge in terms of current \( I \), differential voltage \( dV \), and scan rate \( v \).

\[
Q = \int_{t_1}^{t_2} \frac{dQ}{dt} \, dt = \int_{t_1}^{t_2} I \, dt = \int_{V_1}^{V_2} \frac{dQ}{dt} \, dV = \frac{1}{v} \int_{V_1}^{V_2} i \, dV
\]  

(2)

The total charge passed can be reported as a function of cycle number to demonstrate the stability of the active material; loss in charge storage capacity usually can be attributed to degradation of the electroactive polymer backbone. Conjugated polymers that exhibit capacitor-like charging plateaus in their CV profiles are often studied as active materials for supercapacitors. In this field, the mass-normalized capacitance of the material is seen as a material figure-of-merit. For calculating and reporting an accurate dynamic “capacitance” \( C \) of these pseudocapacitive materials, the charge calculated in Equation 2 can be divided by the voltage window, as shown in Equation 3. Therefore, the voltage window of the redox response is critical for determining important electrochemical properties. For a detailed overview on methods for measuring and reporting capacitance,
especially for redox-active pseudocapacitive materials, the reader is directed to a recent perspective.\textsuperscript{264}

\[
C = \frac{Q}{\Delta V} = \frac{1}{\Delta V} \int_{V_1}^{V_2} I \, dV = \frac{1}{\int_{V_1}^{V_2} I \, dV} \cdot \frac{1}{(V_2 - V_1) \cdot v}
\]  

(3)

In addition to the voltage window, the timescale of the CV experiment is also a highly influential parameter. The scan rate chosen for CV can have a drastic influence on the apparent redox properties of the polymer. For reporting and comparing the general redox characteristics of conjugated polymers, CV should be performed using a scan rate that is fast enough for sufficient signal-to-noise ratios and peak resolution, but slow enough to ensure that the redox process is not limited by diffusional processes. Such diffusional processes could encompass either mass transport (ion diffusion), charge percolation (electron self-exchange in some cases) within the depth of the film, or an interplay of these factors. In many CP films, ion transport is usually regarded as the limiting process, though it can be difficult to distinguish between the two. When diffusions limitations come into play, all of the film does not undergo the redox process in question. Accordingly, the resulting Q is not indicative of the surface coverage of the active material on the working electrode. On this basis, a scan rate of 50 mV s\textsuperscript{-1} was selected for making fundamental comparisons of redox properties.

For evaluating the mass transport limitations associated with the electrochemical doping of various materials, CVs can be performed at variable scan rates. The evolution of the peak current \( i_p \) and symmetry of the redox waves are indicative of different mass transport and/or diffusional limitations. For thin films adsorbed to electrodes (i.e.
“modified electrodes”), the peak current density ($i_p$) is directly proportional to scan rate ($v$) if there are no diffusional limitations in the system.\textsuperscript{245} This proportionality is similar to the relationship observed for purely capacitive currents and indicates that the redox reaction is governed by charge transfer between the electrode and polymer film (i.e. kinetically controlled).\textsuperscript{265,266} When redox processes become diffusion-controlled, the $i_p$ vs. $v$ relation deviates from linearity and adopts a square root dependence with $i_p \propto v^{1/2}$. In such cases, the scan rate dependence of the CV resembles that of Nernstian waves of species diffusing in solution. When performing scan-rate dependent CV, it should be noted that the magnitudes of the overpotentials used can dictate the magnitude of the current response, according to the Butler-Volmer equation.\textsuperscript{267} Therefore, it is important to ensure that the magnitude of the overpotential for oxidation and reduction in the CV are comparable if one seeks to probe fundamental electrochemical characteristics. For instance, when comparing materials with different redox potentials, it is preferable to modify the potential window used in the CV experiments such that the oxidation/reduction overpotential are consistent, rather than simply using the same absolute potential windows for all samples.

To probe the diffusional limitations of some of the polymers presented in this thesis, CV was performed with $v$ ranging from 5–1000 mV s\textsuperscript{-1}. The relationship between $i_p$ and $v$ was used to understand the diffusional limitations associated with electrochemical doping. The transition from a $v$ to $v^{1/2}$ dependence of $i_p$ provides insight into the relative diffusional limitations associated with different polymer structures. Again, it is important to note that such diffusion limitations may originate from any charge transport through the film—whether ionic or electronic. In CPs, the diffusion limitations are typically assumed to be associated with counter-ion transport, though this can depend on the particular polymer-
electrolyte system. Identifying the physical origin of the diffusional process can be difficult, given the electronic and morphological changes that occur with doping, the coupling of ionic and electronic charges in the film, and the coexistence of homogeneous and heterogeneous electron transfer. In non-conjugated redox polymers, the diffusion limitations is usually thought to originate mostly from inter-site redox hopping, i.e. “diffusion” of electronic charges in the bulk of the film. Because these diffusional limitations can be difficult to define unambiguously, an “apparent” diffusion coefficient (D_app) is often provided which captures both ionic and electronic charge transport process in the bulk of the film.

Similarly, monitoring the peak position and average peak position with scan rate can also give insight into the redox process. Shifting of peak positions and/or average peak positions with v may represent ohmic drops in the electrolyte, poor charge transfer between polymer and electrode, and/or counter-ion ion diffusion limitations in the bulk of the film.

The shape of the peaks observed in CVs can also be important for understanding charge formation and interaction in these systems. Classically speaking, asymmetry in redox waves is also indicative of diffusional processes toward and within the active layer. However, in conjugated polymer systems with a broad density of states, several redox processes, the coexistence of multivalent states, and convoluting capacitive effects that occur with conductivity modulation, descriptions of peak symmetry alone are typically not particularly informative for these materials. The width of the redox peak can be related to static variations in activity or standard potentials in the film, with a more heterogeneous distributions of redox sites resulting in voltammetric broadening. Such broadening can also
indicate the presence of interactions between redox centers within the film. Repulsive inter-site interactions cause broadening of redox waves, while attractive interactions tend to “cluster” redox sites together, leading to a narrowing of the voltammetry profile.\textsuperscript{185} In addition, The extent of chain planarity and so-called “\(\pi\)-dimerization” of neighboring chromophores upon doing has also been proposed as an origin of voltammetric broadening observed for \(\pi\)-conjugated oligomers and polymers.\textsuperscript{259,270}

Changes in the voltammetry profile can also be an artifact resulting from of improper casting of films onto button electrodes. Button electrodes used in this work are comprised of an inert conducting rod (e.g. GC) with an exposed surface encased in an insulating plastic body, as illustrated in Figure 2.3.3. Drop-casting solutions on the button electrode can result in films that:

(i) Lie exclusively on the active area (Figure 2.3.3, scheme A)
(ii) Cover the entire active surface, including the seam between the plastic body and active electrode surface (Figure 2.3.3, scheme B)
(iii) Extend beyond the active electrode area and onto the plastic body of the electrode (Figure 2.3.3, scheme B)

As shown in Figure 2.3.3 for an exemplary polymer (“G4-DMP”), these three different drop-casting films can show markedly different CV characteristics. For the films cast improperly according to schemes B and C, the first redox wave is notably suppressed, while the second redox wave appears more prominent, sharper, and occurs at a slightly different redox potential. As described previously, the integrated areas of the CVs can be used as a probe for the overall charge passed during the redox process. Thus, one can also qualitatively see in Figure 2.3.3 that films of G4-DMP cast according to schemes B and C
also pass an overall lower amount of charge relative to an analogous film cast by scheme A, where the polymer film is exclusively on the active area of the electrode and does not extend to the electrode-plastic interface.

The reasons for these differences are complex and will not be discussed in much detail in this thesis. In short, these differences are partly related to the hole mobility modulation upon electrochemical doping and how this transition influences the extent to which the underlying electrode can access polymer coated beyond the active area of the electrode. It is hypothesized here that the relative contribution of hole mobility through the depth of the film and in the plane of the film. This hypothesis is consistent with observations for simulated CVs of PEDOT:PSS showing different peak prominence depending on hole mobility.¹⁹

Because the differences in the CV curves are related to hole mobility, polymers with different transport properties may behave differently than one another if “overcoated” on the electrode. So in addition to distorting the absolute current evolution and charge passed, CVs of polymers cast beyond the active electrode areas (Scheme B or C in Figure 2.3.3) may not even be compared to each other, even if they are all cast in the same manner. For polymers which undergo a substantial enhancement in electronic conductivity upon doping, the polymer can act as an extension of the electrode and access the polymer coated beyond the electrode area. The associated interactions of these redox states may influence both the peak current as well as the sharpness of the redox peaks corresponding to the onset of conductivity. On the other hand, for polymers that do not undergo a sufficient enhancement in electronic conductivity, the “overcoated” polymer that is not in direct contact with the underlying electrode may not electrochemically accessed to any
appreciable degree. Similarly, this would preclude meaningful and quantitative treatment of current and charge densities. In sum, these differences arise (at least in part) in part from the modulation and percolation of mobility and conductivity across different length scales.

Figure 2.3.3 – (Top) Schematic showing different methods for drop-casting polymer solutions onto GC button electrodes (schemes A, B, C), GC planar electrodes (scheme D), and ITO/glass planar electrodes (scheme E). (Bottom Left) Repeat unit structure of G4-DMP. (Bottom Right) Cyclic voltammogram of drop-cast films of G4-DMP (16 μg) in 0.1 M NaCl/H₂O recorded at 50 mV s⁻¹, using various electrodes and drop-casting methods.
An additional complexity arising from surface energy is introduced when films are cast improperly. Casting over both the glassy carbon (or some high surface energy metal) and the low surface-energy plastic body may also induce different film formation dynamics, potentially resulting in different microstructures and redox properties.

While these coating differences may seem trivial, drop-casting onto button electrodes can be extremely difficult to execute properly, especially considering the relatively small active area of most common button electrodes (0.01–0.07 cm$^2$) and the low surface tension of organic solvents used for processing. Based on these variables, the analysis of the relative intensity of the redox waves can be erroneous. In addition, calculation of the mass-normalized redox capacity and charge density (i.e. “charges per ring”) are also subject to error, seeing as the overall charge passed in the CV also can depend on casting technique. The best way to ensure the polymer is only deposited on the active electrode area and does not extend up to or beyond the electrode-plastic interface is to drop-cast in extremely small aliquots and avoid coating the full active area of the electrode, as shown in scheme A of Figure 2.3.3. This technique, however, then calls into practice of normalizing current to the surface are of the electrode when, in fact, the polymer film (which contributes to the vast majority of the current density) does not have a well-defined surface area.

The i-V characteristics of the film cast by scheme A are more capacitive and closely resemble the redox properties of the analogous films drop-cast directly onto GC and ITO planar electrodes, in which there is no insulating plastic body (schemes D and E in Figure 2.3.3). This demonstrates that the previously described differences are, in fact, due to “overcoating” the polymer film beyond the active area of the electrode. Interestingly, the
redox properties do not differ greatly between films cast onto planar ITO/glass and GC electrodes. Small differences in the oxidation onset ($E_{ox}$) may be due to changes in film morphology induced by the rough ITO electrode surface. The enhanced current density observed for the GC planar electrode may be the result of a greater relative contribution from background capacitive charging of the larger GC electrode surface. Notably, the sharpness and breadth of the redox peaks does not depend on the conductivity of the underlying electrode. Given these observations, it is interesting to consider previously reported CVs for identical materials performed on ITO planar electrodes and button electrodes. One can speculate whether the apparent differences are due to electrode effects, processing differences, imprecise casting procedures, or a combination of these influences. In summary, despite the widespread use of CV and scan-rate CV to study electroactive polymer films, there remains some unresolved challenges and inconsistencies associated with film preparation and analysis.

2.3.2 **Differential Pulse Voltammetry**

In addition to CV, differential pulse voltammetry (DPV) is a useful method for characterizing the redox properties of CPs. Like other methods of pulse voltammetry, DPV minimizes the contribution of background charging or capacitive charging currents and enhances the contribution of faradaic currents (i.e. currents arising from a redox reaction). These techniques exploit the fact that capacitive and faradaic currents decay at different rates. In response to a potential step (a “pulse”), capacitive currents decay more quickly with time than faradaic currents. Therefore, by applying a pulse and measuring the current after some period of time, the influence of the capacitive current can be minimized. DPV utilizes a stair-case voltammetry waveform that consists of a larger
pulse (usually 25-100 mV in amplitude) superimposed on a either a linear baseline potential sweep or a series of smaller baseline potential steps across the voltage window of interest.\textsuperscript{273,274} Current is sampled twice: immediately prior to the pulse and at the end of the pulse. A pulse duration is chosen such that the contribution of the faradaic current is maximized relative to the capacitive contribution while still maintaining an appreciable amount of measurable current. The difference in current (hence the use of the term \textit{differential} in DPV) is plotted against the baseline potential.\textsuperscript{245} In well-behaved, single-electron transfer processes, DPV traces yield curves with a single peak centered at the $E_{1/2}$ of the redox couple and a maximum current that is proportional to the concentration or amount of electroactive species under study.\textsuperscript{271,274}

Because DPV enhances the faradaic current while minimizing the capacitive/charging current, this technique and other methods of pulse voltammetry offers enhanced sensitivity to redox species dissolved in a working cell. As such, pulse techniques are often used in sensing applications where enhanced sensitivity and quantification is required, such as in bio-electrochemical sensing.\textsuperscript{275,276}

In the context of studying redox-active CPs, DPV is commonly used to precisely determine the onset of oxidation or reduction ($E_{\text{ox}}$ or $E_{\text{red}}$) of a material. Curiously, the DPV traces of many CPs (like those studied in this work) do not show the typical gaussian profile that is characteristic of classical DPVs. Rather, many DPVs of electroactive polymers resemble the more sigmoidal traces characteristic of other types of pulse voltammetry, like normal pulse voltammetry. While the precise reason for this difference is not entirely clear in the literature, this deviation may be due to a number of factors, such as the presence of
multiple overlapping redox processes and the long relaxation times for capacitive charging of the doped polymer film.

DPV is particularly useful in situations where the background or baseline capacitive current is significant and/or sloping and therefore interferes with the extraction of the redox onset. For electroactive CP films in particular, significant capacitive currents in voltammetric studies are typically not observed until after the onset of doping. Moreover, in many instances the amount of active polymer is not severely limited, so additional material may be deposited on the electrode to enhance the faradaic current, if needed. With these considerations in mind, the onset of faradaic current in a CV of a CP film is frequently sufficiently distinct to precisely determine the oxidation/reduction onset of a material. Nonetheless, DPV is widely considered to be the “gold standard” for determining oxidation and reduction onsets.

In this thesis, DPV is used to extract and report the oxidation onset of polymer films. Prior to DPV measurements, pristine films are cycled through 10-20 full doping-de-doping processes via CV to electrochemically condition the polymer. A DPV sweep is performed across the region where the polymer dopes. The baseline and differential oxidation wave are fit with tangents, with the intercept providing an approximation of $E_{ox}$. DPV was recorded using either an EG&G Princeton Applied Research 273A potentiostat/galvanostat (with CorrWare software) or a Reference 3000 Gamry potentiostat/galvanostat/ZRA (with Gamry Framework 6.5 software).

2.3.3 Redox Stability
The redox stability of CP films upon repeat doping/de-doping is of critical importance to the ultimate utility of these materials in commercially viable electrochemical devices. Unfortunately, there is not a single technique for testing the stability of these materials, nor is there is there a quantifiable observable that is universally used for determining the lifetime of a material or system. The apparent “stability” of a material can be enhanced or diminished depending on the testing conditions chosen and the metrics reported.

Most often, the metrics of stability tests are determined by the target application of the material. For instance, for CPs developed toward ECDs, the electrochromic contrast of a material is typically monitored as a function of cycle number to determine the lifetime of the material, as this parameter is most relevant to the final application. However, other important electrochemical or optical characteristics of a material (e.g. kinetics, oxidation onset) may change before any loss of contrast is observed. Similarly, in the OECT community, a common approach to reporting stability of active materials is to report the drain current transients over repeat on-off cycles to demonstrate the evolution of \( I_{\text{ON/OFF}} \). However, a current transient does not explicitly speak to the evolution of the device transconductance, which is the proposed device figure-of-merit, upon cycling. When discussing the fundamental chemical and electrochemical properties of a material, application-based metrics like contrast, transconductance, etc., may not be the best metrics for studying stability. Many pathways of chemical (electrochemical or photochemical) degradation and/or physical reorganization, which drastically alter the polymer structure and properties, may occur prior to any observed change in the chosen stability metric. Therefore, the fairest evaluations of material stability ought to be made both with respect
to the target application and the underlying (electro)chemistry preceding the loss in performance. Practically speaking, however, the degradation mechanisms of CPs are extraordinary complex, especially in electrochemical devices, where the redox state and composition of the active layer is constantly in flux. Therefore, most stability studies monitor 1-2 relevant variables in lieu of painting a complete picture of the degradation pathway(s).

The method in which stability is tested is also important for making meaningful comparisons of material stability. A CP film can be subject to repeat doping/de-doping cycles in several different manners, over various timescales, and using a range of conditions. For instance, repeat doping/de-doping processes can be accomplished by stepping or sweeping the driving potential between two extreme states. Depending on the frequency of the potential step and/or the rate of the potential sweep, the material in question will spend different amounts of time in its charged state, which is more vulnerable to side reactions and degradation. The potential window of the stability test may also influence the result of the measurement, seeing as greater overpotentials may accelerate degradation. The overpotential in question is particularly important when studying materials with different oxidation/reduction onsets, where using the same absolute potential range may force two different materials into completely different oxidation states. This point will be re-visited in CHAPTER 5. Finally, the choice of electrolyte and environment will also influence stability. Materials studied in degassed and oxygen-free environments likely exhibiting greater stability. In aqueous electrolytes, an additional complication to stability measurements is introduced by pH fluctuations and the generation of reactive oxygen species (e.g. peroxides) during electrochemical cycling that can react
with the active material. Accordingly, the apparent stability of a material studied in an aqueous system can be extremely sensitive to the subtle changes in environmental parameters.

For the work reported in this thesis, several different methods of stability tests were used depending on the target application of the material and the relevant functional conditions. For the ECPs reported in CHAPTER 3, stability tests were performed in a degassed organic electrolyte of TBAPF$_6$ in propylene carbonate (PC) under an argon atmosphere by applying short, sequential square wave pulses between a constant voltage window. Meanwhile, for the OECT active materials reported in CHAPTER 4 and CHAPTER 5, stability was probed by CV cycles performed in an aqueous saline electrolyte system, seeing as these materials are targeted for biological applications. To make more fundamental comparisons of materials and exclude the effect of oxygen, the electrolyte was degassed with argon, even though this environment does not completely represent that of the desired application. For these studies, the total charge passed during the CV was extracted (Equation 2) and reported as a function of cycle number. CHAPTER 5 also includes preliminary data for device stability measurements conducted in ambient conditions using a phosphate buffered saline (pH = 7.4) electrolyte. Here, the transconductance of the device is recorded.

2.3.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful tool used to study different interfacial processes occurring in electrochemical cell, such as electron transfer, mass transport, and capacitive charging. As a frequency-based technique, EIS offers the
ability to separate different phenomena based on their characteristic relaxation times. EIS may also be used to estimate quantities such as resistances, capacitances, inductances, and diffusion coefficients.

2.3.4.1 EIS of Conjugated Polymers

EIS is a highly valuable method for investigating redox processes in electroactive polymers, and it is also quite common. Using EIS, charge and mass transfer kinetics can be de-convoluted from electronic processes. Throughout the last several decades, EIS has been used to probe phenomena such as ionic conductivity, doping/de-doping processes, and charge storage in conjugated polymers. When studying CPs, EIS is highly advantageous for several reasons. First, it gives information about ionic charging and conductivity that other methods cannot provide. Secondly, it is non-destructive and usually requires a small amount of sample, which is important when screening materials produced in small-batch syntheses.

When studying CPs with EIS, most experimental configurations utilize a three-electrode electrochemical cell with a thin film cast onto the WE, similar to the cell presented in Figure 2.3.1. A small AC potential waveform (<10 mV) is applied to a sample, the magnitude of which ensures linear current-voltage characteristics and validates subsequent mathematical analysis. Frequently, a stationary DC offset is superimposed onto the AC bias to “dial in” a particular oxidation state (doping level) in the material under study. The magnitude and phase of the current response can be evaluated as a function of AC frequency and described in terms of a complex impedance \( Z^* \), which is comprised of its real \( Z' \) and imaginary \( Z'' \) components. The phase angle \( \phi \) provides information about
the imaginary component or reactance, which is used to estimate inductive and capacitive processes. In EIS studies of CPs, inductive processes are not particularly relevant, so the reactance is usually exclusively capacitance. The real component $Z'$ provides information about the resistive behavior about the system, while special $Z''/Z'$ relationships can provide information about diffusional processes in electrochemical systems.

In EIS studies, the AC frequency usually ranges from mHz to kHz to capture all relevant processes occurring in cell. It should be noted that traditional (non-electrochemical) impedance spectroscopy uses much higher frequency ranges (MHz–THz) to isolate different processes, such as space charging and dielectric relaxation.

Extracting information from EIS requires the modelling of impedance spectra with equivalent circuits representing the physical processes under study. These equivalent circuit models are governed by fundamental mathematical equations. Basic relationships, mathematics, and circuit analysis governing the interpretation of impedance data will not be presented here (though they are critically important for any individual seeking to perform these studies). The reader is directed to several texts for a more detailed overview of these important fundamentals. For further understanding of EIS as applied to redox-active electrodes and/or CPs more specifically, a number of reviews may be useful.

A variety of equivalent circuit models have been used to describe the behavior of CP films, most of which are based on a modified Randles circuit or a related transmission line model. These models vary with polymer structure, preparation
method, film thickness and uniformity, redox state, electroactivity, cell configuration, and, of course, the user’s own understanding of the system at hand.

In this dissertation, EIS is chiefly used to quantify and compare the steady-state volumetric capacitance (C*) of conjugated polymers. As described previously in CHAPTER 1.3.2.2, the C* of a conjugated polymer is thought to be important for determining the performance of OECT devices. In this context, the capacitance of a material is intended to be a rough quantification of the density of mobile carriers injected into the film over the voltage range of conductivity modulation (i.e. the voltage range of maximum device transconductance). Several different methods can be used to determine the appropriate redox pseudocapacitance, as has been touched on earlier in this section and also outlined in a recent review. Indeed, measuring the capacitance of redox-active polymers is a complex task, and the accepted methods of doing this seem to vary depending on the sub-field. For OECT devices, the relevant C* is typically considered to be a steady-state characteristic rather than a dynamic property. Consequently, EIS seems to the technique of choice for determining C* in OECT active materials.

2.3.4.2 Experimental Protocol

For EIS measurements, polymers films were blade-coated onto clean ITO/glass electrodes, unless otherwise noted. The irregular regions at the film edges were gently removed with a cotton swab, yielding homogeneous and uniform rectangular films. The uniformity of the polymer films is particularly critical in EIS measurements, as the heterogeneity and roughness of a typical drop-cast films can greatly obfuscate film
measurements. For calculating a volume-normalized capacitance $C^*$, a smooth film is also important for accurately the thickness (d) and therefore volume (Vol) of the entire film.

EIS was performed on a Reference 3000 Gamry potentiostat/galvanostat/ZRA controlled with Gamry Framework 6.5 software. The polymer-coated ITO electrode was used as the working electrode, while a large stainless-steel plate serving as the counter electrode and Ag/AgCl electrode (3 M NaCl/H$_2$O inner solution, BASi) was used as the reference. The cell was completed with a 0.1 M NaCl solution in ultrapure water, degassed with argon and kept under an argon blanket throughout the entirety of the EIS studies. The working and counter electrodes were positioned 1 cm apart, with the polymer-coated side of the ITO electrode directly facing the stainless-steel plate. The reference electrode was positioned between the two electrodes at a height such that the reference electrode was not obstructing ion flow between the working and counter. The electrodes were held in place throughout the duration of the study using a custom-built cell cap. A schematic showing the three-electrode cell used in EIS measurements is depicted in Figure 2.3.4A.

Prior to performing EIS studies, the films were electrochemically conditioned via 10 cyclic voltammograms. A 5 mV AC bias was superimposed on a range of DC offsets, which set a particular doping level in the polymer film. Film were held at a given potential for 60 s before recording the EIS spectra to ensure steady-state behavior, starting with the film in its most reduced state and increasing incrementally to its most oxidized state. AC frequencies ranging from 0.1 Hz–1 kHz were used for data collection, while only the low frequency region (0.1–10 Hz) was used for fitting data and extracting C. Data was fit using Zview software (Scribner Associates, Inc.). Upon doping, the fit impedance spectra resulted in an exponent $a \geq 0.80$, which indicates these polythiophenes behave like
imperfect capacitors at low frequencies. Impedance fits were calculated with less than 7% error for each circuit element and $0.0001 < \chi^2 < 0.01$. More details on the equivalent circuit modelling and data extraction can be found in CHAPTER 2.3.4.3.

After EIS, the films were de-doped, rinsed with copious amounts of DI (deionized) water, and dried in ambient conditions. The film thickness, $d$, was measured using a Bruker Dektak XT profilometer. Film thicknesses ranging from 100-200 nm were obtained, typically with a standard deviation of 2-10%, depending on casting method. The film length ($L$) and width ($W$) were measured using calipers, with typical $l$ values ranging from 1.00-2.00 cm and $W$ spanning 0.50-0.70 cm, depending on the film. The capacitance $C$ was obtained by the impedance fits (see CHAPTER 2.3.4.3) and normalized to film volume ($V$), affording the volumetric capacitance, $C^*$, as shown in Equation 4.

$$C^* = \frac{C}{Vol} = \frac{C}{W \cdot d \cdot l}$$

(4)

Unless otherwise noted, error bars reported for $C^*$ values represent the standard deviation of $C^*$ values calculated for 3+ unique films that were cast, measured, and analyzed separately.
Figure 2.3.4 – A) Schematic showing three-electrode cell used for EIS measurements, including working, counter, and reference electrodes (WE, CE, RE, respectively). B) Modified Randles circuit used to fit the EIS data across all frequencies (f), highlighting processes that dominate and low and high frequencies. C) Example Nyquist plot showing EIS data of an exemplary glycol-derived poly(ProDOT) in 0.1 M aqueous NaCl at a DC offset of +0.3 V vs. Ag/AgCl. Arrow indicates increasing f. Black line represents data. Green and yellow lines and text highlight different processes as represented by the Nyquist plot.
2.3.4.3  Data fitting

EIS data for the doped conjugated polymers studied in this work can be modeled using the modified Randles circuit shown in Figure 2.3.4B. The Randles circuit is commonly used in EIS, and it has been employed to extract redox properties of conjugated polymers adsorbed to electrodes.\(^\text{280}\) One line of the circuit consists of an equivalent series resistance (R\(_s\)) that encompasses the resistance of the electrolyte, leads, interconnects, and polymer film, as well as a double-layer capacitor (C\(_{DL}\)) that accounts for double layer (capacitive) charging at the polymer-electrolyte interface. These two elements represent physical processes that dominate the impedance response across the high frequency range (Hz–kHz) (Figure 2.3.4B).

In the impedance formalism, high frequency portion of the complex impedance data manifests as a semicircle in the first quadrant of the Nyquist plot when using common plot conventions (Figure 2.3.4C). The first intercept of the semicircle with the Z’ (real) axis corresponds to the R\(_s\). The second intercept of the semicircle with the Z’ axis represents the sum of R\(_s\) and the charge transfer resistance (R\(_{CT}\)). R\(_{CT}\) accounts for resistance associated with electron transfer across the polymer-electrode interface. The width of the semicircle corresponds to the value of R\(_{CT}\). The peak of the semicircle occurs at a frequency that corresponds to the impedance time constant of an RC parallel circuit, \(\tau_Z\). This relaxation time is equal to the product of R\(_{CT}\) and C\(_{DL}\) (Figure 2.3.4C). The depression and asymmetry of the semicircle are the result of the heterogeneity of the sample and the presence of a distribution of relaxation times. The time constant is also identifiable through characteristic changes in the Bode plots, which show the impedance magnitude (|Z*|) and the phase angle (\(\phi\)) as a function of frequency. Such changes will not be discussed here
further, and again, the reader is directed to more fundamental descriptions of impedance methods for an enhanced understanding.\textsuperscript{277,278}

At low frequencies (~mHz–Hz), the impedance behavior is dominated by the $R_{CT}$ in series with a constant phase element or CPE ($Q_o$, which here redox charging/pseudocapacitance in the film).\textsuperscript{290} These elements are highlighted in the equivalent circuit shown in Figure 2.3.4B. A CPE is a generic element that can be used to model either capacitor, inductor, or resistor with non-ideal properties, such as surface roughness or heterogeneous charging behavior. When the exponent $\alpha$ associated with the constant phase element is close to unity ($0.8 < \alpha < 1.0$), the CPE is thought to represent indicative of capacitive-like behavior and validates the use of the CPE for determining capacitance. The approximate “true” pseudocapacitance $C$ of the polymer film can be directory calculated from $Q_o$ using Equation 5, as described in the literature.\textsuperscript{290,291}

$$C = \left[ Q_o * R_{CT}^{-((\alpha - 1))}\right]^{1/\alpha} \tag{5}$$

This low-frequency redox response of the CP film is manifests as a nearly vertical line along the imaginary $Z''$ axis in the impedance Nyquist plot, as shown for an example of a doped film in Figure 2.3.4C. When this low-frequency line is vertical ($\theta \approx 90^\circ$), the polymer is thought to behave as an increasingly ideal capacitor, and $Q_o$ may even be replaced by a pure capacitor element, $C_o$. If plotted in the complex admittance formalism ($Y*$), the series combination of $R_{CT}$ and $C_o$ yield a semicircle representative of a time constant related to the product of $R_{CT}$ and $C_o$. 
When the polymer is in a partially doped or mass transport-limited regime, the low-frequency regime may manifest as a 45° angle. In such a situation, the data can be modeled either by a $Q_\alpha$ with $\alpha = 0.5$ or a finite-space Warburg element ($W_\alpha$). The Warburg element can also be used to calculate diffusion coefficients of mobile species (in this case, ions) as well as the diffusional pseudocapacitance associated with the redox process. In this work, the Warburg element is not used, although it is frequently used to obtain similar information about pseudocapacitive processes.\textsuperscript{264}

When the polymer is not doped, the low frequency data does not show any capacitive behavior at low frequencies. Therefore, there is no vertical component along the $Z''$ axis of the impedance Nyquist plot, and the low frequency region is instead dominated by entirely by $R_{CT}$. Because the capacitive behavior is of chief interest in this work, only impedance data corresponding to doped/capacitive polymers were fit.

It should be noted that even within the well-defined conditions and theoretical treatment used in this work, there are still several methods one could use for extracting the value of $C$ from the experimental fit. These options, which concern the frequency range of the fitting, are as follows:

(i) Data across the entire frequency range (mHz–kHz) can be fit to the complete circuit in in Figure 2.3.4B. While this approach is arguably the most complete, is not entirely appropriate. First, the high-frequency processes (e.g. $R_{CT}$) are not of significant interest or importance to the conclusions. Secondly, the ITO/glass electrodes exhibit considerable resistance that varies electrode-to-electrode. Therefore, the value of $R_{CT}$ can vary from electrode to electrode and will not
represent the properties of the polymer film. Evaluation of these higher frequency processes would require different electrode materials.

(ii) Only the low frequency data (mHz–Hz) can be fit using a simple R-Q₀ series circuit (highlighted in green in Figure 2.3.4B). This approach gives a representative value of C* across a range of relevant frequencies and takes into account the non-ideal nature of the film via the constant phase element.

(iii) A single frequency can be used to determine the C from the magnitude of the reactance (Equation 6). While this approach is simple, it assumes that the polymer acts as a “perfect” homogeneous capacitor, which is not always true. Also, because this approach only samples a single frequency, it is statistically less powerful than approaches (i) and (ii), which sample a range of frequencies.

\[
C = \frac{1}{2\pi f Z''}
\]  

(6)

Based on the reasoning described above, approach (ii) was used to generate the results reported in this thesis.

2.3.4.4 Considerations

As mentioned previously, EIS is a powerful method for studying electrochemical phenomena. However, interpretation of EIS data is model-dependent and requires both a substantial theoretical background and an appropriate understanding of the sample. In addition, the technique also is highly sensitive to experimental factors, such as electrode set-up and film thickness, which makes comparisons between different samples difficult unless extra caution is taken to ensure known and identical experimental configurations are
used for each measurement. EIS also requires the user to have a solid basis in the fundamentals of the measurement and have an adequate understanding of their sample in order to produce physically meaningful (and accurate) models for data extraction. In fact, it is not uncommon for an equivalent circuit to be selected based solely on literature precedent—regardless of if the systems in question are comparable in their structure or behavior. Occasionally, one may encounter equivalent circuit models that are selected seemingly on the basis of no other reason other than the fact the data fit the model well. This is a practice that should be avoided, as a plethora of different circuit models can fit the same data set if tweaked appropriately.

EIS is among the many ways that the steady-state capacitive behavior of CPs can be evaluated. In the field of OECTs, EIS seems to be the preferred method for extracting the C* of an active material, as it has been suggested that the steady-state C* is most critical for device performance for quantifying charge injection in the transistor channel. However, the low-frequency faradaic pseudocapacitance extracted from EIS is not necessarily exclusively the result of the injection of mobile carriers into the film. As a film dopes and swells at large DC offsets, there is also a possibility of capacitive charging throughout the bulk of the film with a long relaxation time associated with tortuous ion migration. Definitionally, this would not be associated mobile carrier injection, but rather some other physisorption of counter-ions that is characteristic of a porous, three-dimensional conducting electrode. Generally, the capacitive charging contributions are assumed to be minimal. Similar assumptions are made in determining OFET mobility, where it is assumed all charges induced are in fact mobile, when this may not actually be
true. However, it is important for users to take note of this underlying assumption (and its limitations) when establishing property-performance relationships of active materials.

In OECT literature, a single $C^*$ value is typically reported to benchmark materials. The $C^*$ value chosen corresponds to the highest $C^*$ obtained over all DC offsets (doping levels) tested. However, $C^*$ is an evolving property that inherently depends on the doping level of the polymer. Thus, reporting a single $C^*$ value as an intrinsic material property for a material that undergoes redox process is not always appropriate. The highest $C^*$ value does not necessarily correspond to the $C^*$ relevant in OECT device operation. Additionally, in principle, it is not typically best practice to directly relate properties derived from EIS, which is performed using a three-electrode configuration including a reference electrode, to many OECT device configurations that lack a reference electrode. The DC offset in EIS is set relative to a reference electrode, while most OECT device characteristics usually do not incorporate a reference electrode; thus, the potentials cannot be rigorously related.

Moreover, seeing OECTs are typically bias in a manner such that the film exists in a gradient of doping levels,\textsuperscript{188} it is not entirely obvious how a single $C^*$ value obtained for a material in a single doping level would relate to the device properties. Finally, in the OECT literature, $C^*$ is reported normalized to film volume. However, as a polymer is electrochemically doped and uptakes electrolyte, significant swelling can occur.\textsuperscript{292–294} Therefore, it is also unclear which volume (doped or de-doped) is most relevant for normalizing the redox capacity. Lastly, potential thickness-dependence of $C^*$ may render the concept of a “volumetric” capacitance generally invalid. Concepts relating to thickness-dependent optoelectronic, electrochemical, and microstructural properties are not foreign to the field of organic electronics.\textsuperscript{256,295–299} though they may have been forgotten. Thickness
dependence is also difficult to tease out when studying films that are considerably thicker
than the underlying electrolyte itself, as will be discussed more in CHAPTER 5.

Despite all of these considerations which, in principle, limit the relatability of C*(as determined by EIS and normalized to dry film volume) to OECT properties, the C* values for a suite of materials have reported to be proportional to apparent C*, which in turn is reported to be proportional to OECT device transconductance.\textsuperscript{175,201} This may suggest one of three things: (i) that the factors described above, especially relating to doping level and thickness dependence, generally negligible when relating C* to OECT performance, (ii) the series reported in the literature did not span a sufficiently wide range of materials, conditions, or films thicknesses for such effects to manifest, or (iii) extraction of apparent “linearity” from log-log plots, as what has been done in the literature,\textsuperscript{175,201} may mask subtle thickness-dependent effects in these properties. With regards to point (iii), such log-log plots only capture variations across orders of magnitude, while smaller variations collapse onto a linear trend line. Moreover, given the propensity of log-log plots to accentuate small values over larger magnitudes, any potential saturation of C* at large thicknesses may be masked by log-log plots. Given recent studies on the thickness dependence of C* PEDOT:PSS that showed such saturation,\textsuperscript{297} it seems as though scenarios (ii) and (iii) are likely. The field is deeply in need of rigorous metrology to better understand fundamentally important concepts relating to the geometric scaling of OECTs.

2.4 Optical characterization

2.4.1 *UV-Vis-NIR Spectroelectrochemistry*
To monitor electrochemical doping processes, the UV-Vis-NIR absorbance spectra of films were monitored \textit{in situ} as a function of applied potential. This coupled technique, commonly known as spectroelectrochemistry, allows for the study of both of neutral and charged states as the redox reaction unfolds. To configure spectroelectrochemical measurements, polymer films were coated from solution onto a transparent ITO/glass electrode. This was incorporated as the WE into a 3-electrode cell complete with a RE (either Ag/AgCl or Ag/Ag\textsuperscript{+}, depending on the electrolyte), and a CE (a platinum flag). The cell was comprised of a quartz cuvette filled with the electrolyte of choice. For the results presented in CHAPTER 3, spectra were collected using an Ocean Optics USB2000+ fiber-optic spectrophotometer in conjunction with a Pine AFCBP1 bipotentiostat and Aftermath Software. Because this work concerns electrochromic applications in the visible region, spectra were collected from 300–800 nm. For most of the results presented in CHAPTER 4, CHAPTER 5, and CHAPTER 6, spectroelectrochemistry was performed using a Cary 5000 UV-Vis-NIR spectrophotometer in conjunction with an EG&G Princeton Applied Research 273A potentiostat/galvanostat using CorrWare software. For this configuration, spectra were recorded from 300–1300 nm so as to capture optical signatures from charges states while minimizing interference from water that occurs further into the NIR.

Unless otherwise noted, all \textit{in situ} absorbance spectra were recorded after electrochemical conditioning. Spectra were recorded under potentiostatic conditions in 100 mV increments. Before recording the spectra, the film was held at each respective potential for 10–30 s until the current transient reached a steady state.
2.4.2 *Chronoabsorptometry*

Like spectroelectrochemistry, chronoabsorptometry is a method that combines spectroscopic and electrochemical methods to shed light on the redox doping/de-doping of CP films. Chronoabsorptometry involves monitoring the optical density of a CP film at a particular wavelength (or energy) while square-wave potential pulses are applied to film to switch it between its doped and de-doped states. Usually, this technique is performed by monitoring the absorbance corresponding $\lambda_{\text{max}}$ of the neutral $\pi-\pi^*$ transition for a series of pulse lengths (e.g. 60 s, 30 s, 10 s, 5 s, 2 s, 1 s, 0.5 s, etc.). In this experiment, the time-dependent depletion and growth of the neutral $\pi-\pi^*$ transition gives an approximate indication of the rates of doping/de-doping process (also referred to as bleaching/coloration in the context of electrochromism).

In many cases, just monitoring the $\lambda_{\text{max}}$ of the neutral $\pi-\pi^*$ transition does not really tell the “full story” of the doping/de-doping process. Frequently, the neutral $\pi-\pi^*$ transition will shift and/or broaden during the doping reaction, which cannot be captured by monitoring the absorbance at a single wavelength. Also, tracking the depletion of the $\pi-\pi^*$ transition in the visible region does not provide much information about the formation of charged states, which absorb further in the NIR. For instance, a neutral polymer could be doped by: (i) complete conversion first into polarons, which are then converted into bipolarons, (ii) simultaneous conversion into both polarons and bipolarons, or (iii) direct conversion to bipolarons, skipping any polaronic intermediate.

Depending the objective of the study, chronoabsorptometry may also be accomplished by monitoring additional properties (e.g. the absorbance across a range of
wavelengths, the relative intensities of multiple distinct transitions, or even the entire absorbance line shape as a function of time), which can shed more light on the doping process. For instance, CHAPTER 3 utilizes chronoabsorptometry to monitor the integrated absorbance across the entire visible spectrum (380–780 nm), with target applications of black-to-clear electrochromic materials in mind.

When performing chronoabsorptometry, one must be cognizant of a number of variables that can influence the result of the measurement. First, the apparent switching speed is not an inherent material property, as it depends both on the nature of the electrolyte, the underlying electrode, and the experimental configuration (e.g. electrode size and configuration, temperature, potential range). Therefore, if one wishes to compare material systems, it is not advisable to compare chronoabsorptometry results from materials tested in different configurations or using different electrolytes. The proximity, size, and positioning of the counter electrode relative to the working electrode may change the apparent switching speeds of films or may result in an apparent electrochromic “front” that moves across the film and complicate measurement interpretation.

All else being equal, thicker CP films are expected to switch slower than thinner films. Therefore, it is important to define how one wishes to control sample thickness for data acquisition. In the field of electrochromics, films are usually cast to a uniform optical density. While this may result in films with different thicknesses, it is the metric most relevant to the final application and allows for straightforward in-house comparisons between materials. With knowledge of the switching speed and optical density, one can calculate an electrochromic switching time that allows for a rough comparison against other systems. Meanwhile, if the objective of the study is to gain insight to the more
fundamental aspects of electrochemical doping, it is advisable to instead cast films of identical area and thickness, regardless of the final optical density. Films ought to also be cast using similar methods to ensure consistent surface roughness, which could potentially impact the rate of ion transport across the polymer-electrolyte interface.

Just as the potential window influences scan rate-dependent CV characteristics (CHAPTER 2.3.1), the potential window may also impact the apparent optical switching kinetics of ECPs. Greater overpotentials for oxidation and reduction may change the rate at which the film is converted between its doped and de-doped states. Therefore, when comparing materials with different redox potentials (spanning hundreds of mVs), it is advisable to adjust the potential range accordingly.

The chronoabsorptometry results presented in this thesis were collected using an Ocean Optics USB2000+ fiber-optic spectrophotometer in conjunction with a Pine AFCBP1 bipotentiostat and Aftermath Software. The CP film under investigation was spray- or blade-coated onto clean ITO/glass electrodes and configured into a three-electrode electrochemical cell as described previously for UV-Vis-NIR spectroelectrochemical studies (CHAPTER 2.4.1). Pulse durations ranging from 0.25 s – 60 s were used. Depending on the objective of the experiment, these studies involved monitoring either the $\lambda_{\text{max}}$ of the neutral $\pi-\pi^*$ band, the integrated absorbance across the visible region, or the entire absorbance profile across the visible region.

2.4.3 Photography

It is often useful to report photographs of CP films, especially in the field of electrochromism, where the perceived color of the active is of substantial application-level
importance. Photography was performed in a light booth with D50 illumination using a Nikon D90 SLR camera with a Nikon 18-105 mm VR lens. The photographs were recorded of films in a cuvette-sized electrochemical cell while holding the polymer film under potentiation conditions at the indicated potential. Prior to recording photographs, the films were biased at the indicated potential 20–30 s to allow the material to achieve a steady optical state. Photos were recorded after electrochemical conditioning, unless otherwise noted. Photographs are reported without any manipulation apart from photograph cropping and re-sizing.

2.4.4 Colorimetry

To determine the colorimetric properties of the ECP blends studied in 0, the absorbance spectra were converted to CIE $L^*a^*b^*$ coordinates (D50 illumination) using a MATLAB® code. More information about color quantification for this study can be found in CHAPTER 3.2.1.

2.5 Microstructural and Topographical Characterization

2.5.1 Grazing-Incidence Wide Angle X-Ray Scattering

In the field of organic electronics, grazing-incidence wide angle X-ray scattering (GIWAXS) is the most common technique for studying the microstructural ordering in thin films. GIWAXS relies on the elastic scattering of X-rays with the sample under study. This tool can provide information about lattice spacing, relative degrees of crystallinity, coherence length, grain/domain size, texture, or even qualitative differences in the extent and nature of long-range (meso- and micro-scale) “order” in CP films. More detailed
discussions surrounding the use of GIWAXS for studying polymer films (especially in the context of organic electronics) can be found in the literature.301–308

2.5.1.1 General Principles

A schematic depiction of a typical GIWAXS experiment is shown in Figure 2.5.1. GIWAXS involves irradiating a thin film sample with an incident beam of X-rays (k_i) at a very shallow incident angle (θ_i). The value θ_i is selected such that it is only slightly greater than the critical angle (θ_c), below which total external reflection occurs. In this configuration with θ_i > θ_c, k_i penetrates tens to hundreds of nanometers into the film and probes the “bulk properties of the material. For experimental configurations where with θ_i > θ_c, the fine surface structure of materials can be studied. Measurements with high signal-to-noise ratios and reduced acquisition time typically require a synchrotron source to generate k_i.

The periodic arrangement of polymer segments (e.g. repeat units, cofacial π-stacks, and/or lamellae) the film gives rise to Bragg diffraction that can be detected at a range of angles and directions. An X-ray plate detector is placed at a relatively small distance away from the sample (10–50 cm) to capture scattered X-rays (k_f) diffracted at wide angles. In this configuration, scattering intensity is measured as a function of scattering angle and direction. The scattering angle (2θ_s) of k_f is related to the wavelength of the X-rays (λ) though the a quantity known as the scattering vector (q), as shown in Equation 07.301
Figure 2.5.1 – A) Schematic depiction of a GIWAXS experiment, showing exemplary 2D scattering pattern in the \((q_{xy}, q_z)\) plane. B) Unit cell of a regioregular P3HT crystallite (as adapted with permission from Kurta et al.\textsuperscript{309}), showing edge-on orientation (left), and face-on orientation (right), and corresponding lattice and scattering notations.

Under conditions of constructive interference by Bragg diffraction, \(q\) is inversely proportional to the lattice spacing \((d_{hkl})\) of the particular feature with Miller indices \((hkl)\)
(Equation 7). Hence, the scattering vector \( q \) is said to quantify “reciprocal space” and exists as a Fourier transform of the “real space” lattice.\(^{310}\) In other words, \( q \) in reciprocal space represents a periodicity in real space.

\[
q = \frac{4\pi}{\lambda} \sin \theta_s = \frac{2\pi}{d_{hkl}}
\]  

(7)

While the scattering angle \( \theta_s \) gives information about the lattice spacing of the scattering feature, the scattering direction depends on the texture of the scattering feature. When scattering vector is parallel to the substrate (\( q_{xy} \), sometimes referred to as \( q_r \)), the scattering pattern represents periodicity in the direction of the sample plane. Similarly, when the diffraction plane is perpendicular to the substrate (\( q_z \)), the scattering pattern represents order occurring normal to the substrate. GIWAXS is commonly presented yielding two-dimensional maps, like that shown in Figure 2.5.1A, which shows scattering intensity in the \((q_{xy}, q_z)\) plane.

In a prototypical conjugated polymer, regioregular P3HT (rr-P3HT), the crystalline domains assemble according to the unit cells shown in Figure 2.5.1B. When a rr-P3HT crystallite is arranged such that the \( \pi \)-stacking direction \((0k0)\) is in the plane of the substrate, the orientation is referred to as “edge-on.” In this orientation, diffraction from \( \pi \)-stacking is observed along the horizontal \( q_{xy} \) axis. Note that given the unit cell shown in Figure 2.5.1B (adapted from the literature\(^{309}\)) as well as interpretations found in the field for both PTs and PXDOTs,\(^{311–314}\) the reflection corresponding to a single \( \pi \) stack is denoted as \((020)\). Meanwhile, complementary lamellar stacking \((h00)\) is normal to the substrate, scattering from lamellae occur predominantly in the \( q_c \) direction. In the “face-on” orientation (Figure
2.5.1B), π-stacking direction (0k0) is in normal to the substrate, the resulting scattering from π-stacking and lamellae occur in the $q_z$ and $q_{xy}$ directions, respectively. It should be noted that the scattering in the “true” $q_z$ direction is not really probed in WAXS experiments due to the curvature of the Ewald sphere of diffraction. As such, presentation of GIWAXS data usually shows a missing “wedge” in the $q_z$ direction. So, while this region is experimentally inaccessible, the breadth of scattering peaks around the $q_z$ axis is sufficient for making inferences about the out-of-plane periodicity. Orientation of crystallites or diffracting species at intermediate textures results in scattering features diagonally in the $(q_{xy}, q_z)$ plane.

Constructive interference from scattering may manifest as “smeared” arcs or as discrete, sharp spots in the $(q_{xy}, q_z)$ plane, as shown schematically in Figure 2.5.2. Highly isotropic samples where all textures are represented more or less equally result in a broad scattering arc across all polar angles $\chi$ (where $\chi$ is defined as the angle between the scattering vector and the substrate normal),$^{301}$ as shown in Figure 2.5.2A. Diffracting species with a stronger preferred orientation usually appear as discrete spots within a relatively narrow range of $\chi$ (Figure 2.3.4B-C).

Studying the broadening of the scattering vector can shed light on the coherence length ($L_c$) and paracrystallinity parameter ($g^*$) of the diffracting species, which encompasses the cumulative disorder in a system.$^{301,307}$ The overall scattering intensity can be loosely related the degree of order in the system (assuming similar scattering cross sections/film thicknesses). In some sense, this treatment is similar to analogous measurements of “extents of crystallinity” in polycrystalline solids. In polymeric systems, however, scattering may also originate from aggregates with sufficient long-range order.$^{315}$
However, shorter-range aggregates, which are highly influential for dictating optical and electronic properties, may not result in prominent scattering detected by GIWAXS. Hence, developing a complete description of the extent and nature of “order” in CP films usually requires one to: (i) define the length scale of order that is relevant for the process under study, and (ii) use complementary techniques (e.g. thermal and optical methods) to fully understand and compare systems.

Figure 2.5.2 – Schematic depictions of crystallite texture (top), expected scattering from (100) reflections (middle), examples of corresponding GIWAXS patterns (bottom). Each depiction is provided for a sample with: (A) mostly isotropic texture, similar to a powder diffraction pattern (B) oriented texture, and (C) highly oriented texture. Figure has been reprinted with permission from Rivnay et al.\textsuperscript{301} © 2012 American Chemical Society.
In the field of organic electronics, GIWAXS is commonly regarded as a necessary component of thin film analysis, even though analyses of the scattering patterns may not be entirely relevant or complete in their descriptions. Moreover, GIWAXS analysis of new materials is particularly challenging, as there are no established unit cells from which to base assignments. While the scattering characteristics of P3HT are widely studied, there can also be ambiguity in discerning between (\(0h0\)) reflections, (\(00l\)) reflections, and scattering from so-called “side chain interactions,” as these can show similar q values. Making simple changes to the structure of P3HT processing can result in drastic changes in the GIWAXS pattern arising from backbone twisting, even for similar processing conditions. Additional complexities are introduces when studying doped systems where lattice parameters may shift, and when characterizing copolymers, where the registry of stacked chains introduces additional reflections. Many GIWAXS analyses are “best guesses” that, without more in-depth studies, should not be used for strong arguments about a material’s structure or properties.

### Measurement details

GIWAXS samples were prepared by coating polymer films from solution onto polished Si wafers. Prior to coating, wafers were scored and diced into squares (~ 3 cm × 3 cm) and cleaned as previously described (CHAPTER 2.2.2). The particular solution coating method for each sample is indicated in the discussion presented in subsequent chapters.

Most GIWAXS measurements were performed at the Stanford Synchrotron Radiation Lightsource on Beamline 11-3. Use of the Stanford Synchrotron Radiation
Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The sample was irradiated with an incident beam $k_i$ energy of 12.7 keV with a sample distance of 250 mm and $\theta_i$ was equal to 0.13°. Data was collected on a MAR345 image plat detector using sample exposure times up to 300 s, depending on the signal from the sample. Some GIWAXS patterns (as indicated in CHAPTER 5, for polymer OH-DMP) were collected at beamline 11-BM (Complex Scattering Materials) of the National Synchrotron Light Source II at Brookhaven National Laboratory (a U.S. Department of Energy Office of Science User Facility operated for the DOE Office under Contract No. DE-SC0012704). For these samples, the $k_i$ energy was 13.5 keV, and the $\theta_i$ of the measurement was 0.12°. The sample distance was approximately 259 mm. Scattering patterns were calibrated using a standard sample of LaB$_6$.

Raw data from GIWAXS experiments were processed using software packages WAXStools and Nika in IgorPro (version 6.37). Two-dimensional intensity vs. q-spacing files were corrected for detector geometry. Intensities are represented on a linear color scale. For line-cuts, images were reduced to 1D plots with a sine correction via integration of out-of-plane $q_z$ cake segments ($5^\circ < \chi < 20^\circ$) and in-plane $q_{xy}$ cake segments ($70^\circ < \chi < 85^\circ$), and intensity was scaled to film thickness for all polymers except OH-DMP in CHAPTER 5. For OH-DMP, out-of-plane ($0^\circ > \chi > -15^\circ$) and in-plane ($85^\circ > \chi > 70^\circ$) line cuts were arbitrarily normalized, as this film was collected under a slightly different geometry at a different beamline. The GIWAXS pattern of polymer p(g6T2-T) in CHAPTER 4 was also arbitrarily normalized, as these films were too soft for thickness measurements by profilometry. For these materials (OH-DMP and p(g6T2-T)), the
scattering pattern still provides information about the lattice spacing and coherence length of the diffracting regions, but no information can be extracted from the scattering intensity.

Line-cuts were analyzed using the peak fitting feature in Origin Pro 2019. D-spacing for Miller indices \( d_{hkl} \) were calculated using Equation 7. In Equation 7, \( q \) is the scattering vector quantity corresponding to the peak scattering intensity in the line cut. The average correlation length \( L_C \) was calculated from the modified Scherrer analysis in Equation 8, assuming a shape factor of 1.\(^3^{01}\)

\[
L_C = \frac{2\pi}{\Delta_q}
\]

(8)

Here, \( \Delta_q \) is the full width at half maximum for the scattering peak in the line-cut. The paracrystallinity parameter \( g^* \) was calculated by Equation 9, as given in previous literature.\(^3^{02}\)

\[
g^* = \frac{1}{2\pi} \sqrt{\frac{\Delta_q d_{hkl}}{\Delta_q d_{hkl}}}
\]

(9)

All representative GIWAXS patters correspond to a reproducible result that was obtained from multiple (2+) films, cast and measured separately. Lattice spacing correspond to the average of the spacing obtained from measuring multiple samples. Uncertainty values in lattice spacing represent the standard error obtained from multiple measurements.
2.5.2 Atomic Force Microscopy

In CHAPTER 5, tapping-mode atomic force microscopy (AFM) is used to study the topography and surface roughness of CP films. AFM is a non-destructive scanning probe technique used for characterizing surface properties and interactions. AFM is commonly used for studying the topography of thin films. This technique does not, however, provide information about the morphology or composition of a film. To prepare samples for AFM, polymer films were blade-coated onto clean Si wafers and treated as described in the text. Height and phase images were collected in standard tapping mode (~150 kHz) with a Bruker Dimension Icon AFM using a Bruker RTESP-150 probe (Part: MPP-12100-10, spring constant = 5 N m⁻¹).

2.6 Organic Electrochemical Transistors

The details concerning OECT device operation and measurements are discussed in CHAPTER 1.3.2. In this thesis, OECT characteristics from both so-called “planar” and “interdigitated” devices are presented. A planar device consists of a single rectangular planar channel framed by two simple S and D contacts, while an interdigitated device consists of S and D contacts that are of two interlaced, comb-like electrodes that are separated by a much smaller distance.

2.6.1 Planar OECTs

Planar OECT devices were sourced and measured by collaborators in the group of Jonathan Rivnay at NU, as reported in the literature. These device results apply only to planar devices with polymer G3-DMP, as specified in CHAPTER 4. OECT devices were
fabricated photolithographically\textsuperscript{324} by collaborators at NU and sent to GT for coating with G3-DMP. Prior to coating, the OECT device was rinsed with isopropanol, dried under a stream of N\textsubscript{2} gas, and cleaned for 10 minutes in a UV-O\textsubscript{3} chamber. A solution of G3-DMP in chloroform (10 mg mL\textsuperscript{-1}) was blade-coated on the substrate at room temperature using an aluminum blade with a gap height of 1250 \textmu m and a blade speed of 75 mm s\textsuperscript{-1}. After casting, devices were returned to Northwestern University for further testing.

A mechanical peel-off of the sacrificial parylene layer allowed for a dry patterning of the active material while leaving the underlying passivating parylene layer intact. The samples were rinsed gently with DI water prior to testing. The devices were wired in the common source configuration with an Ag/AgCl gate electrode (Warner Instruments) and an electrolyte of 0.1 M NaCl in DI H\textsubscript{2}O. Planar OECT device characterization (transfer and output I-V curves) was performed on a National Instruments PXIe system (equipped with a NI-PXI-4143 SMU and a NI-PXI-6289 DAQ) using custom LabView software. OECT mobility approximated using a frequency dependent approach (bandwidth matching), as explained in the literature.\textsuperscript{201,325}

2.6.2 *Interdigitated OECT*

Interdigitated OECT devices were prepared and measured at Georgia Institute of Technology. Devices fabricated in such a configuration are susceptible to enhanced contact resistance.\textsuperscript{205} Accordingly, these device characteristics should only be used as a rough test of the functionality of the device and may not be used to make benchmark or compare any systems. This holds true especially for devices fabricated with short channels and relatively high performing systems (where the contact resistance dominates the measurement).
Results from this configuration cannot be used for in-house comparisons of said systems, evaluation of geometry scaling, or benchmarking against planar OECT devices. More rigorous approaches are required for such studies.

Active layers were fabricated by blade- or spray-coating polymer films onto interdigitated platinum electrodes obtained from MicruX Technologies (electrode model ED-IDE1-Pt with 90 pairs of interdigitated electrode arms, 10 μm arm length, 10 μm electrode length, Pt thickness ≈ 150 nm, active area = 9.6 mm², average width = 2.75 mm). Thickness values of dry, de-doped films were measured using a Bruker Dektak XT profilometer. Film thickness values ranged from 80–300 nm with a large standard deviation (~20–40%) given the rough underlying passivation layer coating the MicruX electrode. Prior to device testing, excess polymer was removed from the electrode by gently wiping with a cotton swab.

Figure 2.6.1 shows the system developed at Georgia Institute of Technology for testing interdigitated OECTs. Contacts to the source and drain electrodes were made using an MicruX-AIO batch cell testing platform. The batch cell was filled with 1× PBS in ultrapure water (18.2 MΩ·cm). A chloridized Ag wire (Ag/AgCl) was suspended in the electrolyte solution and used as a gate electrode. The cell was connected to an Agilent 16422a test fixture which was controlled by an Agilent E5263A 2 Channel IV Analyzer equipped with two source measure units (SMUs, Agilent E5291A and E590A). One of the Pt pads (source, S) was set to the ground unit (GNDU) of the Agilent E5263A, while the other planar Pt pad (drain, D) was connected to the Agilent E5290A. The Ag/AgCl wire (gate) was connected to the Agilent E591A. Force and sense connections for all three terminals were connected separately.
Figure 2.6.1 – Configuration developed for testing of interdigitated OECT devices. A) Parameter analyzer, highlighting SMUs used for drain and gate terminals and GNDU used for source terminal. B) Test platform, which connects the OECT cell to the parameter analyzer. The gate, source, and drain connections for force (F) and sense (S) signal lines are labeled. C) Zoom-in of interdigitated OECT device in the cell and interdigitated area coated with a poly(ProDOT) active material. Illustration of interdigitated electrode has been adapted from the supplier. © 2020 MicruX technologies.

For generating the transfer and output curves reported in this thesis, transistor characteristics were collected using a Keysight Easy Expert software with a custom I-V
sweep/step configuration. Devices were tested under ambient conditions. Data were collected for at least three separate devices (cast and measured separately) to ensure reproducibility. The transfer and output curves presented in this thesis represent those recorded after at least three electrochemical doping/de-doping cycles in the transistor configuration to condition the films. Representative output curves were collected with a \( V_D \) step size \(-1 \text{ mV}\), a delay time of \(0.02 \text{ s}\), and a hold time of \(3 \text{ s}\), scanning \( V_G \) every \(-50 \text{ mV}\) and starting in the de-doped “off” state. Representative transfer curves were collected using a \( V_D = -0.45 \text{ V}\) with a hold time of \(3 \text{ s}\), a delay time of \(0.02 \text{ s}\), and a \( V_G \) step size of \(-1 \text{ mV}\), starting in the de-doped “off” state. The transconductance \( (g_m) \) was calculated from the from I-V characteristics of the transfer curves using the Equation 1. Error bars represent the standard deviation for the characteristics extracted from at least three devices with active layers cast and measured separately, unless otherwise noted.

Due to the instability associated with the Ag/AgCl gate electrode, the stability of OECT devices (in terms of \( g_m \) retention) was tested using a different device configuration. Here, the AIO batch cell \( S \) and \( D \) contacts was attached to a Pine AFCBP1 bipotentiostat (Aftermath software, DEVC, window mode) and used as working 1 (WE1) and working 2 (WE2), respectively. The cell was filled with \( 1\times \text{PBS} \) and equipped with a Ag/AgCl single-junction RE and a Pt flag CE. Repeat transfer curves were generated at ambient conditions by sweeping WE2 from \(-0.5 \text{ to } +0.5 \text{ V}\) vs. Ag/AgCl \((v = 50 \text{ mV s}^{-1})\) with a WE1-WE2 offset potential (analogous to a \( V_D \)) of \(-0.2 \text{ V}\). Electrolyte was replaced every 1–2 h to prevent concentration fluctuations. Note that this connection uses a different biasing scheme, no distinct force/sense connections, and a \( V_D \) offset that more closely corresponds to the linear regime. Because this configuration was performed on an older instrument and
therefore was subject to enhanced noise, the I-V characteristics of the transfer curve were smoothed using in Origin Pro 2019. The smoothed data was differentiated to calculate the approximate \( g_m \).

2.7 Neutron Reflectivity

Neutron reflectivity measurements were performed to evaluate changes in the thickness, composition, and interfacial roughness of CP films upon exposure to electrolyte and electrochemical doping. A brief, surface-level overview of neutron reflectivity will be presented here, as needed to provide a basis for understanding results presented in CHAPTER 6. For a more in-depth discussion surrounding the physics of neutron reflectivity and applications thereof, the reader is directed to external sources.\(^{327-331}\)

The experiments outline here were supported by the Spallation Neutron Source (SNS), a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. Studies were performed under the user proposal IPST-22018. The Neutron Sciences Directorate at ONRL solicits proposals such as these twice per year.

2.7.1 General Principles

The penetrating ability of neutrons makes neutron scattering techniques immensely valuable for characterizing internal structures and interfaces of multi-layer that are “buried” within solid or liquid assemblies. Neutron reflectivity is useful for investigating the thickness, roughness, and composition of thin layers normal to the sample surface and over a large horizontal sampling plane. Neutron reflectivity involves irradiating a sample with a columnated beam of neutrons \( k_i \) with a known incident angle \( \theta_i \) and wavelength \( \lambda \) (Figure
The way incident neutrons interact with the sample depend on the particular nuclei comprising the sample. The scattering length density (referred to as SLD here, but sometimes denoted as \( N_b \)) of a sample dictates the nature of the interaction of the neutron beam with the sample. This quantity, in combined with \( \lambda \), dictates the neutron refractive index of a sample. Thus, the SLD is the origin of contrast in neutron scattering measurements.

The SLD of the material depends on its density (\( \rho \)) and the bound coherence scattering length (\( b \)) of the atoms comprising the sample, as described in Equation 10.

\[
SLD = \frac{\rho N_A}{M_M} \sum_{i}^{n} b_i
\]

In most reflectivity experiments, like those presented in this work, the scattering vector \( q \) of the incident neutrons is varied by changing the \( \lambda \) and \( \theta_i \). These quantities are related in the same manner they are related for X-ray scattering (Equation 7). If a monochromatic neutron beam is used, then \( q \) is varied only by changing \( \theta_i \). A schematic depiction of a reflectivity study on a simple bilayer system in air is presented in Figure
2.7.1A. This system consists of a thin film, “Layer 1”, with a thickness \( d = 20 \text{ nm} \) and a non-specified SLD, “SLD (1)”. Layer 1 is on top of a thicker layer, “Layer 2,” with \( d = 100 \text{ nm} \) and a non-specified SLD, “SLD (2)”. The entire assembly is in air.

![Experimental Configuration](image)

![Reflectivity Pattern](image)

![Compositional Profile](image)

**Figure 2.7.1** – Scheme for neutron reflectivity studies, showing A) general experimental geometry on a simple two-layer system with no interfacial roughness, B) theoretical reflectivity profile for the two-layer system, labeling Kiessig fringes and critical edge, and C) resulting SLD thickness profile extracted from the reflectivity data.
In this configuration, only secularly reflected neutrons $k_f$ are detected, where the angle of incidence and scattering are equal ($\theta_i = \theta_s$). This specular condition is what restricts the information provided by neutron reflectivity to the normal direction of the sample. When the value of $q$ corresponds to a value less than or equal to the critical angle of the sample, total external reflection occurs. In this case, virtually all the neutrons are reflected, so the recorded reflectivity ($R$) for this range of $q$ is simply equal to 1. As $q$ moves above the critical edge (shown as a yellow dot in Figure 2.7.1B), neutrons penetrate into the sample ($k_t$) and the recorded reflectivity falls below 1. The overall decay of $R$ with $q$ after the critical edge scales with $q^{-4}$ (so-called “Fresnel reflectivity”).\(^{327}\) The position of the critical edge in $q$ space is related to the SLD difference between the fronting and incident medium (air and Layer 1, respectively, in Figure 2.7.1A). Therefore, fitting the critical edge of reflectivity data is important for first establishing the SLD of a sample. Once the penetrating neutrons $k_t$ have transmitted through Layer 1, these neutrons will encounter the interface between Layer 1 and Layer 2. At this point, some neutrons will be reflected, while others will penetrate further into Layer 2.

The constructive and destructive interference of neutrons reflected from the various interfaces gives rise to distinct peaks in the $R$ vs. $q$ plot. These patterns, known as Kiessig fringes, provide a wealth of information about the sample under investigation. The spacing of the fringes in inversely related to the thickness of the layers. For example, reflection from the bilayer in Figure 2.7.1 yields thick fringes from the Layer 1 superimposed on thin fringes from Layer 2. Qualitatively speaking, the height of the fringes is related to the SLD contrast across the reflecting interface, and the dampening of the fringes with $q$ gives an indication of interfacial roughness/diffuseness. Depending on the number and orders of the
multi-layer, the available contrast, and the interfacial characteristics, very complicated reflectivity patterns can be obtained.

The reflectivity data can be modelled by mathematical formalisms,\textsuperscript{330} the complexities of which will not be discussed here. Modelling of reflectivity data yields extract depth-dependent compositional information about samples, where the apparent SLD can be profiled in the z direction. As shown in Figure 2.7.1C, fitting of the reflectivity data from a bilayer in air will give a compositional trace with steps at the SLD of air, “SLD (1)”, and “SLD (2)”. These depth profiles are typically how the most relevant and useful information is extracted from reflectivity studies.

2.7.2 Measurement Details

Reflectometry was performed at the Liquids Reflectometer (LR, beamline 4B) at the SNS at ORNL. The LR at the SNS is a horizontal, time-of-flight reflectometer. The reflectivity data were collected using a sequence of 3.25 Å-wide continuous wavelength bands (selected $\lambda = 2.63 \text{ Å} < \lambda < 16.63 \text{ Å}$) and incident angles (ranging over $0.60^\circ < \theta_i < 2.71^\circ$). The scattering experiment employed a specular geometry, where $\theta_i = \theta_s$. The momentum transfer vector ($q$, as related to $\lambda$ and $\theta$ by Equation 7) was varied over a range of $0.008 \text{ Å}^{-1} – 0.220 \text{ Å}^{-1}$. Reflectivity curves ($R$ vs. $q$) were obtained by combining seven different wavelength ranges and angle data sets together, maintaining a constant sample footprint and relative instrumental resolution of $\delta'q/q = 2.4\%$ by varying the incident beam apertures. Each reflectivity experiment involved a data acquisition time of approximately 45–90 min, depending on the sample environment.
Reflectivity patterns were recorded for:

(i) Dry and unmodified electrodes (Au-coated Si wafers) in air
(ii) Dry polymer-coated electrodes in air, pristine and as-cast
(iii) Polymer-coated electrodes (pristine) immersed in an electrolyte at open circuit voltage ($V_{oc}$), prior to any applied bias, after 90 minutes of exposure.
(iv) Polymer-coated electrodes immersed in an electrolyte after electrochemical conditioning, under potentiostatic conditions in the fully de-doped state
(v) Polymer-coated electrodes immersed in an electrolyte after electrochemical conditioning, under potentiation conditions at various doping levels

Samples were prepared as previously described in CHAPTERS 2.2.2.5 and 2.2.6. For dry sample measurements, reflectivity experiments were performed in ambient conditions with a scattering orientation incident to the top of the sample. For in situ measurement performed, the polymer-coated WE was configured into a custom three-electrode electrochemical cell with a Pt CE, an Ag/AgCl RE, and an anodized aluminum body. The cell used for in situ reflectometry is shown schematically in Figure 2.7.2. Prior to recorded the NR profile of the biased films, the current transient in the potentiostatic experiment was allowed to reach a steady state close to 0 mA to ensure that the polymer had equilibrated to the electrochemical conditions. Typically, this process required 5–20 seconds. The potential was maintained throughout the duration of the beam calibration and the NR experiment.
In this cell, the RE and CE electrodes were separated by a round Teflon-coated O-ring (thickness = 1 mm, inner diameter = 49 mm inner). Once assembled, the cell was backfilled with electrolyte solution through the lurer lock feed through. The electrolyte was prepared by combining volume fractions of ultrapure H$_2$O and D$_2$O with NaCl salt, yielding an overall electrolyte concentration of 0.5 M NaCl. The RE was placed into the cell through one of the lurer lock ports used for electrolyte loading and contained by the O-ring. The contacts were made to the WE, CE, and RE using a combination of copper tape (which contact the WE and CE along the perimeter without interfacing with the electrolyte) and commercial alligator clips. Photographs showing the assembly of the cell are presented in

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Figure 2.7.2 – Illustration of electrochemical cell used for in situ neutron reflectivity measurements. Reprinted with permission from Browning et al. © 2020 American Chemical Society.
Figure 2.7.3. The complete cell was mounted directly onto the beamline and controlled using a Biologic VSP and EC-Lab software. Notably, the scattering orientation orientated was changed such that the beam was incident to the bottom of the substrate.

Figure 2.7.3 – Photographs depicting the step-wise assembly of the electrochemical cell used for in situ neutron reflectivity studies. A) Polymer-coated WE with Cu tape contacts on a plastic wafer case. B) WE loaded into the base of the cell, secured in place with pins, and loaded on a steel mounting plate. C) Teflon O-ring placed on WE. D) A Pt-coated wafer, used as the CE, lying face-down on top of the cell and secured by a screw. E) Cell body with Teflon cap and two lurer lock ports for loading electrolyte. F) Fully assembled electrochemical cell, showing alligator clips contacting WE, CE, and RE.

2.7.3 Data Fitting

Reduction of neutron reflectivity data was performed on-site a reduction algorithm developed by scientists at ORNL, generating $R$ vs. $q$ plots with $\delta R$ corresponding to error
from Poisson statistics. Reflectivity models and fits were developed using the Motofit package\textsuperscript{335} in Igor Pro 8.04. The bare substrates were modelled first, followed by the fitting of the dry, as-cast films on the electrodes to extract relevant information about the thicknesses and SLDs for the multi-layer system. For modelling the rest of the data (from the in situ experiments), constant parameters (such as the SLD, roughness, and thickness of Au, Cr, Si, etc.) were either fixed at their initial value or confined to a range of ±5–10\% of their initial value. Fitting was performed with pre-established models representing the system and modified if necessary. The model parameters were adjusted to first match the $R$ vs. $q$ profile of the critical reflectivity edge and scattering background, then manual modifications were made to minimize the chi-squared $\chi^2$ of the fit within reason. Once manually minimized, a more optimized fit of the existing model was obtained by through the genetic algorithm in Motofit (>1000 iterations, fit tolerance = 0.001). The resulting fits were used to extract three key parameters for each layer in the system: layer thickness, SLD, and roughness. These fits were used to generate SLD vs. $z$ profiles, which prove a one-dimensional representation of the heterostructure composition normal to the substrate.
CHAPTER 3. CONJUGATED POLYMER BLENDS FOR BLACK TO-TRANSMISSIVE ELECTROCHROMISM

This chapter has been adapted with permission from the previously published manuscript\textsuperscript{238} (© 2018 Wiley-VCH):


3.1 Introduction

3.1.1 Motivating the Development of Black-to-Transmissive ECPs

Electrochromic materials that reversibly switch between black and transmissive states are highly sought-after in a number of commercial and military applications, including energy-saving dimmable windows, user-controlled protective eyewear, and optical privacy shutters. In addition, black electrochromes are useful for communicating text and complex images \textit{via} reflective displays in electronic paper devices, wearable “smart glasses,” and transmissive panel monitors. The ultimate utility of such materials depends on their ability to repeatedly transition between two optical states in a rapid, on-demand fashion.

Electrochromic $\pi$-conjugated polymers (ECPs) are a class of electrochromic materials that offer an appealing platform for the realization of true black-to-transmissive electrochromism. ECPs can undergo full colored-to-colorless transitions on rapid time
scales (often in second to sub-second regimes for multi-centimeter square films),\textsuperscript{122} with high coloration efficiencies, contrasts ($\Delta\%T$ at $\lambda_{\text{max}}$) up to 70%, switching stability over thousands to hundreds of thousands of cycles,\textsuperscript{104} and in many cases, colored states that can be refreshed by a small current or voltage pulses.\textsuperscript{122,336} As explained in CHAPTER 1.3.1, ECPs can also be readily tuned for color through straightforward chemical modification of the polymer backbone. The addition of solubilizing aliphatic or polar side chains allows for these materials to be processed as electronic inks in low-cost and large-scale processing techniques, such as inkjet-printing, along with blade-, spray-, and slot die coating.\textsuperscript{123,124,337–342} In recent years, a deeper understanding of the structure-property relationships that control color and switching properties has enabled the development of extensive libraries of cathodically coloring polymers. These materials have been successfully integrated into plastic\textsuperscript{124,343,344} and paper-based\textsuperscript{125,126,345,346} electrochromic devices, making them promising candidates for flexible or transient electronic displays.

While most colored-to-transmissive ECPs have $\pi$-electronic structures that have been carefully modified to absorb specific wavelengths of visible light to achieve highly saturated colors, a black ECP must absorb across the entire visible spectrum in its colored state. Meanwhile, the transmissive state must absorb as little visible light as possible in the same wavelength range for optimal contrast and optical clarity. Developing a material that undergoes such drastic spectral changes upon application of an electrical bias presents a unique materials design challenge. An additional complexity arises when seeking to develop black-to-transmissive electrochromic materials that can transition through intermediate shades of gray, as well.

\textbf{3.1.2 Previous Approaches}
A number of strategies have been invoked in pursuit of black-to-transmissive ECPs. For instance, synthetic approaches have targeted polymers with backbones designed for broad absorption of visible light. Beajuge et al. reported the first black-to-transmissive ECP using a cathodically coloring random copolymer of 3,4-propylenedioxythiophene (ProDOT) donor and 2,1,3-benzothiadiazole (BTD) acceptor moieties. Two properties of this polymer led to broad absorption across the visible region. First, BTD-based donor-acceptor polymers are characterized by a dual absorbance at long and short wavelengths, which inherently absorb more visible light than most traditional all-donor polymers that exhibit single absorbance bands within the visible region. Second, the random nature of the copolymerization lead to varying combinations of donor and acceptor along the polymer backbone, each of which absorb in different regions of the visible spectrum. Further optimization of the donor-to-acceptor feed ratio yielded a black-to-transmissive ECP (herein referred to as “ECP-Black”) that absorbed broadly across the visible range with various accessible hues of black. This so-called “donor-acceptor approach,” which involves copolymerizing electron-poor and electron-rich monomers, has since been employed to yield other black ECPs. Broad absorption across the visible range has also been achieved in alternating donor-acceptor (DA) polymers by incorporating multiple acceptors along the backbone such as benzoquinoxaline, benzoselenadiazole, and benzotriazole. Beyond donor-acceptor systems, cobalt-based supramolecular metallo-polymers have been pursued as black-to-clear electrochromes. A salient example involves a Co(II)-bisterpyridine metallo-supramolecular polymer that switches between a highly transmissive, pale yellow neutral state and a broadly absorbing state upon electrochemical reduction. Another interesting approach was demonstrated by Sassi et al. in 2016, where
a small molecule Weitz-type chromophore, which absorbs at short wavelengths, was tethered onto an EDOT-ProDOT copolymer that absorbs at longer wavelengths, yielding a black-to-clear ECD. A final family of materials that have demonstrated broadly absorbing colored states are triphenylamine (TPA)-based polymers. Through structural tuning, an anodically coloring TPA with a black oxidized state and a colorless neutral state was recently developed. Despite this progress, many of these systems do not offer sufficiently broad spectral coverage, especially in the high- and low-energy ends of the visible region. In particular, many cathodically coloring systems often suffer from tailing of the NIR-absorbing charge carrier bands into the visible region, leaving a slight blue tint in the transmissive state.

Given the challenges associated with developing a color-neutral and high optical contrast material, an alternative approach toward black-to-transmissive electrochromism is to blend vibrantly colored chromophores whose collective absorption entirely covers the visible spectrum. This can, in theory, be accomplished using the three traditional subtractive primaries, cyan, magenta, and yellow (CMY), whose respective absorbance bands span the low-, mid-, and high-energy regions of the visible spectrum, or by two-component combinations of dual-band and mid-gap absorbers, such as green and magenta. Previous work has demonstrated such color mixing principles in stacked or complementary black-to-transmissive electrochromic devices as well as by solution co-processing of individual cathodically coloring chromophores into a single optically active layer. To demonstrate the ability to finely control the hue through color mixing, our group has previously utilized solution co-processing of multi-component ECP blends to tune the dynamic brown coloration in electrochromic eyewear. This blending approach is also
advantageous when targeting black-to-transmissive switching, as it allows for facile tuning of optical properties without requiring new material synthesis or complex electrode architectures. In particular, solution co-processing offers a great deal of versatility and predictability and can readily be adapted to yield different hues of black by simply tuning the mass ratios of the constituent ECPs.

Blending electrochromes for black-to-transmissive switching, however, demands special consideration of the evolution of the color change with applied electrochemical potential. For applications such as dimmable fenestration and eyewear, where it is desirable to dial in intermediate shades, bleaching and coloration should proceed through color neutral gray tones rather than vibrantly colored intermediates. Developing an ECP blend with such properties requires that the constituent chromophore bleach within a similar voltage window and in a concerted fashion. However, because the color of an ECP is determined by the effective conjugation length (which is multi-dimensional in nature) and the extent of π orbital overlap in response to various steric, electronic, and intermolecular effects, any attempt to manipulate the color will often also result in a change in the electrochemical properties of the material. Consequently, while it may be relatively straightforward to find a combination of ECPs whose collective absorption profiles cover the visible range, it is much more challenging to also ensure that the redox properties of the components coordinate to bleach and re-color at identical potentials and similar rates. To date, no study has demonstrated how to control both the extreme and intermediate coloration of black-to-transmissive ECP blends.
3.1.3 Color-Mixing by Solution Co-Processing

In this work, solution co-processing is presented as a means for overcoming the many challenges associated with high-contrast black-to-transmissive electrochromism. We demonstrate how the composition of ECP blends can be strategically tailored to access a range of black hues with complete coverage of the visible spectrum, enhanced redox stability, and achromatic optical transitions to visibly transmissive states. Utilizing a collection of five soluble ProDOT-based copolymers, we expand subtractive color mixing beyond the traditional CMY model and report a series of three-component black ECP blends. By including a green and a new orange colored-to-colorless polymer (developed by Dr. Dylan Christiansen) in our mixing scheme, we can control the colored states, intermediate hues, and long-term coloration of black-to-transmissive ECP films. With integrated contrast across the visible spectrum exceeding 40%, these materials are significantly more color-neutral than our previously reported ECP-Black and can be tuned for achromatic optical transitions.

3.2 Results and Discussion

3.2.1 Color Quantification

Because the perception of color can be highly subjective and qualitative, it is important to be able to quantify the exact hue of various colors for valid comparisons. The human eye has three types of cone cells that are sensitive to unique wavelength ranges of light; if the total spectral power distribution of light is weighted to account for this relative sensitivity, three effective stimulus values are generated. These three values can objectively quantify a color. Quantification of chromaticity can be accomplished in the CIE $L^*a^*b^*$ coordinates.
coordinate system, where a three-dimensional space defines the chromaticity and luminosity of a color. Here, $L^*$ represents the lightness of a color, where 0 is black and 100 is diffuse white. The $a^*$ and $b^*$ axes ($\pm 128$) represent the relative saturation of four quaternary colors: red ($+a^*$), green ($-a^*$), blue ($-b^*$), and yellow ($+a^*$) (Figure 3.2.1). Because the $L^*a^*b^*$ color space is bound and non-uniform, it does not behave the same as a vector space. Thus, the ability to perform mathematics on color space coordinates is heavily restricted.

Figure 3.2.1 – Three-dimensional CIE $L^*a^*b^*$ color space, highlighting a cross sectional ($a^*, b^*$) plane. The region around the origin in the ($a^*, b^*$) plane corresponds to relatively achromatic colors.

A vibrant color with high degree of saturation will have large $a^*$ and/or $b^*$ values, such as Coca-Cola Red$^{364}$ ($L^*=53, a^*=80, b^*=59$) or Buzz Gold$^{365}$ ($L^*=73, a^*=12, b^*=77$). A truly achromatic color (e.g. black, gray) can be accessed when a material's absorbance, combined with the nonuniform spectral sensitivity of the human eye, evenly attenuates the
intensity of visible light. Achromatic shades have relatively equal contributions from each of the four chromatic components and therefore map to low \((a^*, b^*)\) coordinates. A black-to-clear electrochromic material with intermediate grey shades would ideally only exhibit a variation of \(L^*\) upon switching. The color chromaticity \((C_{ab}^*)\) represents the overall hue of the color and is defined as the magnitude of the vector in the \((a^*, b^*)\) plane, as indicated by Equation 11. Color-neutral shades (e.g. black and gray) have equal contributions from each of the quaternary chromatic components and therefore are associated with low \(C_{ab}^*\) values. For this work, the \(C_{ab}^*\) will be a chief metric for quantifying the color neutrality of samples.

\[
C_{ab}^* = \sqrt{(a^*)^2 + (b^*)^2}
\] (11)

3.2.2 Constituent ECPs

When blending polymers to achieve a color neutral black, five dioxythiophene-based polymers were selected from our group’s collection of colored-to-colorless ECPs. These ECPs readily dissolve in toluene and can be co-processed from solution into homogeneous electrochromic films. Each blend was formulated to include a high-gap absorber (ECP-Yellow or -Orange), a mid-gap absorber (ECP-Magenta), and dual-band DA polymer (ECP-Cyan or -Green) with strong absorption bands in both the low- and high-energy ends of the visible spectrum. Not only does this color mixing scheme offer a means toward materials with broad spectral coverage in the colored state, but it also allows for the high-, mid-, and low-energy absorption intensity of the blend to be independently
manipulated, which is important when fine-tuning the blend composition to a desired achromatic state. In addition, we show that the intermediate colored states and the switching performance can be manipulated by changing the constituent chromophores. Following this model, three different black blends were formulated: a conventional CMY blend (comprising ECP-Cyan, -Magenta, and -Yellow), a CMO blend (ECP -Cyan, -Magenta, and -Orange), and a GMO blend (ECP-Green, -Magenta, and -Orange), as shown schematically in Figure 3.2.2.

Figure 3.2.2 – Repeat unit structures of ProDOT-based conjugated electrochromic copolymers used for subtractive mixing strategies for accessing black. $R = 2$-ethylhexyl. Figure has been reprinted with permission from the literature.© 2018 Wiley-VCH

The redox and optical properties of the individual blend components are summarized in Table 3.2.1, with the corresponding spectra and redox characterizations shown in Figure 3.2.3. Figure 3.2.3A-C show the neutral state spectra of the individual ECPs as well as their composite blend spectra, and Figure 3.2.3D compares the cyclic
voltammograms of the blend components. The noteworthy differences between the two high gap absorbers (ECP-Yellow and ECP-Orange) and the two low gap absorbers (ECP-Green and ECP-Cyan) are their distinct onsets of oxidation ($E_{ox}$, determined by DPV as shown in Supporting Figure 3.4.1) and the potential required to reach the transmissive state ($E_{clear}$). $E_{clear}$ is determined spectroscopically and corresponds to the potential above which we observe no further change in the level of transmittance in the visible range upon further oxidation. The potential-dependent absorption spectra for the various blend components used in this study are shown in Supporting Figure 3.4.3. These differences, as we will show, have a substantial impact on the electrochromic switching properties and intermediate coloration of blended ECPs.

Table 3.2.1 – Redox and optical properties of ECPs used in developing black-to-clear blends.

<table>
<thead>
<tr>
<th>ECP</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$E_{ox}$ (V) vs. Fc/Fc$^+$</th>
<th>$E_{clear}$ (V)$^b$ vs. Fc/Fc$^+$</th>
<th>($a^<em>, b^</em>)^c$</th>
<th>Contrast at $\lambda_{max}$$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECP-Yellow</td>
<td>465</td>
<td>+0.47</td>
<td>+0.7</td>
<td>+9, 76</td>
<td>60</td>
</tr>
<tr>
<td>ECP-Orange</td>
<td>468</td>
<td>+0.18</td>
<td>+0.5</td>
<td>+29, +68</td>
<td>65</td>
</tr>
<tr>
<td>ECP-Magenta</td>
<td>544</td>
<td>+0.12</td>
<td>+0.3</td>
<td>+59, -16</td>
<td>70</td>
</tr>
<tr>
<td>ECP-Cyan</td>
<td>406, 687$^a$</td>
<td>+0.22</td>
<td>+0.6</td>
<td>-30, -15</td>
<td>50$^d$</td>
</tr>
<tr>
<td>ECP-Green</td>
<td>458, 672$^a$</td>
<td>+0.13</td>
<td>+0.5</td>
<td>-36, -2</td>
<td>50$^d$</td>
</tr>
</tbody>
</table>

$^a$ Denotes low-energy charge-transfer band for DA polymers ECP-Cyan and ECP-Green.

$^b$ Reported to the nearest 0.1 V.

$^c$ Contrast is measured for films coated to a transmittance of %T = 10% ± 2% at $\lambda_{max}$

$^d$ Contrast is reported for the low-energy absorbance band.

$^e$ Reported for fully reduced, de-doped film.
The absorbance of ECP-Yellow and ECP-Orange have similar $\lambda_{\text{max}}$ values, but the line shape of ECP-Orange is slightly more broadened, as shown in Figure 3.2.3 (a direct comparison can be found in Supporting Figure 3.4.4). This spectral difference, though minor, results in a significant difference in perceived color. This can be explained by the photopic response of the human eye. The increased spectral coverage of ECP-Orange encompasses a region of the visible spectrum where the human eye is most sensitive to changes in the wavelength (~480–520 nm). Therefore, subtle differences on the low-energy side of the absorbance spectra of these materials are exaggerated when these materials are viewed by the human eye, resulting in noticeably different perceived colors. This is reflected by the large difference in the $a^*$ values associated with the reduced states of the two ECPs (Table 3.2.1).

When comparing the redox properties of ECP-Orange and ECP-Yellow, the difference in the oxidation potential likely arises from a combination of both steric and electronic effects. In ECP-Yellow, the high degree of aromaticity of the benzene ring and the bulkiness of the ethylhexyloxy groups obstruct planarization to a quinoidal geometry in the oxidized state, giving rise to the high $E_{\text{ox}}$ (Figure 3.2.3D) and $E_{\text{clear}}$ potentials (Supporting Figure 3.4.3). The 3,4-dioctylthiophene co-monomer used in ECP-Orange, on the other hand, is inherently easier to oxidize than the phenylene unit in ECP-Yellow, likely due to the decreased aromatic stabilization and increased electron richness associated with the thiophene heterocycle. This results in a higher HOMO energy and, consequently, a lower $E_{\text{ox}}$. By replacing the 3,4-alkoxy functionalized thiophene units in ECP-Yellow with 3,4-propylenedioxy-functionalized analogues in ECP-Orange, the solubilizing groups are
further away from the conjugated backbone, which also may decreases the steric hindrance associated with intrachain planarization and intermolecular interactions. The backbone of ECP-Orange, being exclusively composed of thiophene-based repeat units, also allows for an anti-configuration between rings, i.e. the 3 and 4 positions between neighboring rings are antiperiplanar, which in turn reduces inter-ring strain and allows for greater backbone planarization in the neutral state compared to ECP-Yellow. This perhaps allows the oxidized state of ECP-Orange to more easily assume a quinoidal bonding structure, which stabilizing NIR-absorbing charge carriers and resulting in a lower $E_{\text{clear}}$ compared to ECP-Yellow.

When evaluating the two low-gap components, ECP-Green and ECP-Cyan, the difference in $E_{\text{ox}}$ is the result of the higher relative ratio of the electron-rich (ProDOT) to the electron-poor (BTD) moieties in ECP-Green. This increase in electron-richness destabilizes the HOMO level of ECP-Green relative to ECP-Cyan, resulting in a decreased $E_{\text{ox}}$, as well as cathodically shifted redox peaks in the cyclic voltammograms, as shown in Figure 3.2.3D. The higher ProDOT content in ECP-Green also facilitates planarization and charge carrier delocalization, leading to a 0.1 V lower $E_{\text{clear}}$ (Table 3.2.1). The optical properties of ECP-Cyan and ECP-Green are fairly similar, as both exhibit a dual band absorbance profile characteristic of many donor-acceptor polymers. The band at longer wavelengths arises from a transition between a delocalized HOMO and a LUMO localized on the acceptor, while the short wavelength absorption band originates from a charge transfer transition between the HOMO and the LUMO+$n$ orbital localized on the donor unit. By increasing or decreasing the donor content, the position of the high-energy band can be readily red- or blue-shifted, whereas the low energy band is less sensitive to the
donor-to-acceptor ratio. The higher ProDOT content in ECP-Green results in a red-shifting of the high-energy band of this ECP by about 50 nm relative to ECP-Cyan, whereas the low energy band is blue-shifted only by 15 nm. This significant shifting of the high energy band results in ECP-Green absorbing more in the middle of the visible spectrum (450–500 nm) and less at the extremes when compared to ECP-Cyan.

Figure 3.2.3 – Superimposed absorbance spectra of individual electrochromic polymer components and blends (black lines) of (A) Cyan-Magenta-Yellow, (B) Cyan-Magenta-Orange, and (C) Green Magenta-Orange. (D) Superimposed cyclic voltammograms of ECPs blended in this study, performed on drop-casted films on glassy carbon electrodes in 0.5M TBAPF₆/PC. Figure has been reprinted with permission from published literature.© 2018 Wiley-VCH
3.2.3 **Black ECP Blends**

To make color-neutral blends, the relative amount of each ECP was adjusted such that resulting films exhibited relatively uniform spectral coverage and low chromaticity ($C^*_{ab} < 5$) in the colored state (Figure 3.2.3 and Table 3.2.1). As shown in Table 3.2.1, each of the three-component ECP blends are significantly more color-neutral than the random copolymer ECP-Black ($C^*_{ab} = 16$) which has a slight purple hue and a higher negative $b^*$ (see spectra in Figure 3.2.4 and photographs in Figure 3.2.6).

The enhanced color neutrality of the CMY, CMO, and GMO blends can be attributed to their broadened and more uniform absorbance across the visible spectrum, especially below 450 nm and above 750 nm, where these blends absorb more effectively than ECP-Black (Figure 3.2.4). The different ratio of blend components is due to subtle differences in the absorbance spectra of each of the ECPs. For instance, when comparing CMY with CMO, the absorption band of ECP-Orange is broader with respect to that of ECP-Yellow, so the CMO blend requires less of the mid-gap chromophore ECP-Magenta to achieve color neutrality. Similarly, the high-energy absorption band of ECP-Cyan is blue-shifted relative to that of ECP-Green. As a result, in the GMO blend the absorbance of ECP-Orange and the high-energy band of ECP-Green overlap more closely than ECP-Orange and ECP-Cyan in the CMO blend. To compensate, the amount of ECP-Orange was reduced four-fold in the GMO blend, compared to the CMO blend. Finally, ECP-Cyan absorbs more low- and high-energy light than ECP-Green, which impacts the blend in two ways. First, because the high- and low-energy absorption bands are brought closer together in ECP-Green, slightly less of the mid-gap absorber (ECP-Magenta) relative to the dual band-absorber is required to formulate the GMO blend than the CMO blend. Second, CMO
and CMY blends have broader spectral coverage than the GMO blend, however GMO is still very color-neutral ($C_{ab}^* = 3.3$), as the human eye is least sensitive to the light transmitted at the extreme ends of the visible spectrum.

Table 3.2.2 – Mass ratios, color coordinates, and chromaticity of evaluated ECP blends and ECP-Black.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass Ratios</th>
<th>Colored State</th>
<th>Transmissive State</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L*  a*  b*</td>
<td>L*  a*  b*  C_{ab}^*</td>
<td>L*  a*  b*  C_{ab}^*</td>
</tr>
<tr>
<td>Blend CMY</td>
<td>10.0, 4.0, 2.0</td>
<td>45.1  2.5 -1.0  2.7</td>
<td>82.1 -7.1 -1.5  7.3</td>
</tr>
<tr>
<td>CMO</td>
<td>10.0, 4.0, 4.0</td>
<td>40.1  4.4 -1.3  4.6</td>
<td>81.5 -4.7 -4.8  6.7</td>
</tr>
<tr>
<td>GMO</td>
<td>10.0, 3.4, 1.0</td>
<td>37.7 -1.7 -2.8  3.3</td>
<td>81.7 -4.6 -6.1  7.6</td>
</tr>
<tr>
<td>ECP-Black</td>
<td>--</td>
<td>40.0 -3.1 -15.7 16.0</td>
<td>84.2 -5.4 -4.7  7.1</td>
</tr>
</tbody>
</table>

When oxidized to their colorless states, the transmittance spectra of the blends all follow a similar trend across the visible, with each material transmitting the greatest amount of green-yellow light (500–600 nm) as shown in Figure 3.2.4B. For electrochromic materials, contrast is often evaluated as the change in transmittance between the reduced and oxidized state at a single wavelength. For broadly absorbing hues like black, it is more descriptive to define contrast as the change in integrated transmittance across the entire visible spectrum, which spans from 380–780 nm according to CIE standards. Among the blends, the CMY film has the lowest integrated transmittance in the colorless state, presumably due to the reduced electrochromic contrast of ECP-Yellow when compared to ECP-Orange, especially above 650 nm (Supporting Figure 3.4.4), as well as the larger
relative amount of ECP-Cyan. While both the CMO and the GMO can reach a similar level of transmittance in the oxidized state, the higher integrated contrast of the CMO blends is a result of the broader spectral coverage in the colored state. While ECP-Black has the highest integrated transmittance in the oxidized state, it does not have the highest integrated contrast. This can be explained by ECP-Black’s colored state, which has a relatively narrower absorption profile in the visible range than the blends in the visible region, leading to a higher integrated transmittance at 0.0 V. Each of the blends exhibited an integrated contrast greater than or equal to that of ECP-Black (40%) across the entire visible spectrum, with the CMO blend having the highest integrated contrast (45%) among all black materials evaluated (see Table 3.2.3).

Figure 3.2.4 – Superimposed absorbance (A) and transmittance (B) spectra for ECP-Black (black lines), CMY Black (yellow lines), CMO Black (orange lines), and GMO Black (green lines) in the oxidized state (+0.8 V) and reduced state (0.0 V). Dashed lines denote the limits of the visible spectrum (380-780 nm). Potentials reported vs. Ag/Ag+ reference electrode. Figure has been reprinted with permission from published literature.238 © 2018 Wiley-VCH
While each blend studied has a unique composition, their electrochemical properties do not differ much. As demonstrated in Supporting Figure 3.4.5, the CMO, GMO, and CMY blends and ECP-Black all pass similar amount of current and require a comparable charge to switch between the colored and colorless states (Table 3.2.3). Each black formulation undergoes a broad oxidation within a potential window ranging from +0.1 V to +0.8 V. The $E_{\text{ox}}$ for each blend occurs around +0.08 V (Table 3.2.3), while ECP-Black begins oxidizing at +0.02 V vs. Fc/Fc$^+$. Interestingly, the CMY, CMO, and GMO blends all oxidize at slightly lower potentials than any of their constituent ECPs, suggesting that there are intermolecular interactions in these blends that may result in the formation of polymer domains that are easier to oxidize. However, a more important property for these cathodically coloring blends is the $E_{\text{clear}}$. As expected, the CMY blend has the highest $E_{\text{clear}}$ as a result the ECP-Yellow component, which bleaches at the highest electrochemical potential. The GMO blend exhibits the lowest $E_{\text{clear}}$ of the blends, which is not surprising, as it is comprised of the three ECPs with the lowest $E_{\text{clear}}$ values. When evaluating the kinetics of the black-to-transmissive transition, the CMO and GMO exhibit similar switching times when stepped between -0.5 and +0.8 V and can complete a full transition in 2 s when tested in this particular configuration (as shown in Supporting Figure 3.4.6). The CMY blend exhibits slightly slower switching kinetics using this same potential step, most likely due to high oxidation potential of ECP-Yellow, which has been previously observed for brown ECP blends.\textsuperscript{362}
Table 3.2.3 – Electrochromic and electrochemical properties of black blends and ECP-Black.

<table>
<thead>
<tr>
<th></th>
<th>ECP-Black</th>
<th>CMY Blend</th>
<th>CMO Blend</th>
<th>GMO Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>%T (+0.8 V)(^a)</td>
<td>61</td>
<td>51</td>
<td>56</td>
<td>57</td>
</tr>
<tr>
<td>%T (0.0 V)(^a)</td>
<td>21</td>
<td>11</td>
<td>12</td>
<td>17</td>
</tr>
<tr>
<td>Integrated Contrast (%)(^a)</td>
<td>40</td>
<td>40</td>
<td>45</td>
<td>40</td>
</tr>
<tr>
<td>(E_{\text{ox}}) (V)(^b)</td>
<td>+0.02</td>
<td>+0.08</td>
<td>+0.08</td>
<td>+0.09 V</td>
</tr>
<tr>
<td>(E_{\text{clear}}) (V)(^c)</td>
<td>+0.5</td>
<td>+0.7</td>
<td>+0.6</td>
<td>+0.5</td>
</tr>
<tr>
<td>Charge to Switch (mC cm(^{-2}))(^d)</td>
<td>3.3</td>
<td>4.1</td>
<td>3.6</td>
<td>3.7</td>
</tr>
</tbody>
</table>

\(^a\) Transmittance and contrast are reported as integrated across the visible spectrum (380 – 780 nm).

\(^b\) \(E_{\text{ox}}\) is reported relative to the Fc/Fc\(^+\) couple.

\(^c\) \(E_{\text{clear}}\) is reported to the nearest 0.1 V vs. the Ag/Ag\(^+\) reference, which was calibrated against the Fc/Fc\(^+\) couple \((E_{1/2} = +65 \text{ mV})\).

\(^d\) Charge to switch was calculated by integrating the CV from the black state (0.0 V vs. Ag/Ag\(^+\)) to \(E_{\text{clear}}\).

3.2.4 Long-Term Coloration

To evaluate the functional lifetimes of the CMY, CMO, and GMO blends, each film was repeatedly stepped between the colored (-0.5 V) and colorless (+0.8 V) state 1,000 times. After approximately 100 switches, the CMY blend lost almost 10% of its overall integrated contrast (Supporting Figure 3.4.7). This loss in contrast is attributed to the electrochemical instability of ECP-Yellow component, which has been demonstrated in previous work.\(^{133}\) As shown in Supporting Figure 3.4.8, the \(b^*\) value of the CMY blend
decreased from about $b^* = -1.5$ to $b^* = -17$ over 1,000 switches, corresponding to a loss in yellow chromaticity and increased blue coloration. By substituting ECP-Yellow for ECP-Orange in the CMO and GMO blends, the switching stability can be greatly improved, as ECP-Orange is able to maintain its full optical contrast over 1,000 redox cycles.$^{104}$ Over the course of 1,000 switches, the CMO and GMO blends exhibit minimal change in overall chromaticity and remain relatively color-neutral (Figure 3.2.5), demonstrating that both the CMO and the GMO are robust electrochromic systems.

Figure 3.2.5 – Chromaticity for ECP black blends recorded over 1,000 redox switches between -0.5 V and +0.8 V vs. Ag/Ag$^+$ reference electrode. Spectra were obtained every 100 cycles while holding the potential at -0.5 V and +0.8 V. Redox cycling was performed under an argon blanket in 0.5 M TBAPF$_6$/PC. Figure has been reprinted with permission from published literature.$^{238}$ © 2018 Wiley-VCH.
3.2.5 *Intermediate Coloration*

By incorporating ECPs with a diverse set of redox properties and coloration kinetics, solution co-processing offers the unique possibility of directly controlling the chromaticity of the optical evolution. In certain applications, such as for windows or eyewear, it is desirable to be able to access for color-neutral intermediate shades. For other uses, such as on-off displays or optical shutters, it is more important that the switch between the extreme states occurs rapidly and with little detectable transient chromaticity. Following this motivation, both the intermediate and transient optical properties of the ECP films were studied.

To study their intermediate chromaticity, the ECP films were incrementally oxidized in 0.1 V steps ranging from 0.0 V (black state) to +0.8 V (transmissive state). At each potential, the visual appearance (Figure 3.2.6A-D), CIELAB coloration (Figure 3.2.6E), and absorption spectra (Supporting Figure 3.4.3) were evaluated. In doing this, we evaluate which colors between the extreme states can be “dialed in” under intermediate potentiostatic conditions. As shown in Figure 3.2.6A, ECP-Black transitions from a blue-purple color to a transmissive state through light blue intermediates. The color coordinates associated with this process maintain low $a^*$ and $b^*$ values throughout the transition as shown in Figure 4E. In the case of the CMY blend (Figure 3.2.6B), the $E_{clear}$ mismatch between ECP-Cyan, -Magenta, and -Yellow results in vibrantly colored intermediate states. At +0.2 V, ECP-Magenta has reached a fairly colorless state while ECP-Cyan and ECP-Yellow remain fully colored, as evidenced by the strong absorptions bands below 500 nm and above 600 nm in the potential-dependent spectra (Supporting Figure 3.4.9). This residual absorption results in the film exhibiting intermediate shades of green with $(a^*, b^*)$
values that deviate greatly from the achromatic origin of the CIELAB color space (Figure 3.2.6E). Above +0.6 V, ECP-Cyan is oxidized to its transmissive state, leaving ECP-Yellow as the only colored component remaining in the film until it finally bleaches at +0.8 V. Similarly, the CMO blend undergoes a strongly colored optical evolution from the black to the transmissive state. In the CMO blend (Figure 3.2.6C), ECP-Magenta and ECP-Orange are oxidized to a transmissive state within a narrow potential window whereas ECP-Cyan remains colored until +0.6 V, giving rise to a vibrant cyan intermediate state with \( L^* = 66, a^* = -16, \) and \( b^* = 7 (C_{ab}^* = 17.5) \) between +0.4 and +0.5 V. ECP-Green, on the other hand, having a lower \( E_{ox} \) and \( E_{clear} \) than ECP-Cyan, reaches its colorless state at a potential that more closely aligns with the \( E_{clear} \) of ECP-Magenta and ECP-Orange. Matching the \( E_{clear} \) of each ECP component in the GMO blend results in a more concerted bleaching process and a more color-neutral optical evolution. While the color of the GMO film appears slightly green at +0.3 V (\( L^* = 55, a^* = -16, b^* = 7, C_{ab}^* = 17.5 \)), the overall transition is not nearly as vibrant as the CMY or CMO blends because of the lower \( L^* \). The reason for the residual green hue at +0.3 V is that ECP-Magenta (Supporting Figure 3.4.3), unlike ECP-Green, switches from a vibrant colored state to a fairly clear state within a narrow potential window, rather than gradually bleaching out as the oxidation process progresses. This result demonstrates that measuring and reporting \( E_{clear} \) is perhaps even more important than the \( E_{ox} \) especially when it comes to developing ECP blends. Because each component in the GMO blend has a relatively low \( E_{clear} \), this formulation reaches a fully transmissive state at +0.5 V, which is much lower than the potentials required to reach similar optical states in the CMY and CMO blends (Table 3.2.3).
Figure 3.2.6 – A-D) Photographs of ECP-Black (A), the CMY blend (B), the CMO blend (C), and the GMO blend (D) taken under potentiostatic conditions. Each photograph is taken at 0.1 V increments, increasing from 0 V to +0.8 V vs. Ag/Ag+ in 0.5 M TBAPF$_6$/PC. E) The corresponding color coordinates for ECP-Black and the various blends at 0.1 V increments. Figure has been reprinted with permission from published literature.© 2018 Wiley-VCH

3.2.6 Transient Coloration

When switching the blend films rapidly between the reduced and oxidized states (on/off switching), there may also be detectable transitional colors as the film evolves from its extreme black and transmissive states. This transient coloration is determined by not only the redox potentials of each component, but also by the kinetic factors associated with the bleaching of each chromophore, which depend on factors such as overpotential, charge carrier interconversion, and ion transport. To evaluate the nature of the transitional colors when switching between black and transmissive states, a square wave bias of -0.5 V to +0.8 V was applied to the CMO and GMO films and spectra were recorded every 0.1 s to capture the nature of the direct optical evolution from the black to the transmissive state.
For both the CMO and GMO blends, the first 0.4 s after oxidation is associated with a drastic decrease in the absorbance in the mid-range of the visible spectrum (500–550 nm), as shown in Figure 3.2.7A, as a result of the rapid bleaching of ECP-Magenta. In the later stages of bleaching, contributions from ECP-Cyan and ECP-Orange dominate the spectra of the CMO Blend. Because the high-energy band of ECP-Cyan does not overlap much with the absorbance of ECP-Orange, the combined absorbance of these components results in rather even coverage of the visible spectrum in the later stages (0.5–1.0 s) of the optical evolution. This is illustrated by the colored rectangles in Figure 3.2.7A, which show the spacing of the ECP-Cyan and ECP-Orange absorbance bands during the transitional coloration. Because the high-energy absorbance band of ECP-Green is red shifted with respect to that of ECP-Cyan, the absorption band of ECP-Green has a greater overlap with ECP-Orange. This can be seen schematically in Figure 3.2.7B from 420–490 nm, highlighted by the green and orange bars. As a result of this overlap, the spectral evolution assumes a distinct, uneven curvature with reduced absorbance around 500 nm, which indicates that the GMO blend bleaches through slightly green-tinted shades when transitioning directly from the black state. The minimal overlap of these bands in the CMO blend results in a more color-neutral optical evolution from the black to the transmissive state. Once ECP-Magenta has reached a colorless state in the GMO blend, the remaining transition is characterized by the bleaching of ECP-Green and ECP-Orange.
Figure 3.2.7 – Spectral evolution of (A) CMO blend and (B) GMO blend when applying a square wave potential from -0.5 V to +0.8 V (vs. Ag/Ag⁺) in 0.5 M TBAPF₆/PC. The black line represents the absorption spectra of the films in the reduced state at the time of the pulse, while the lightest gray line represents the spectra 1.5 seconds after applying the square wave. Spectra was recorded every 100 ms. Superimposed on the spectra are colored bands corresponding to the absorption maxima and full width at 75% peak max. of the individual ECP components: ECP-Cyan (cyan rectangles), ECP-Magenta-2 (pink rectangles), ECP-Orange (orange rectangles), and ECP-Green (green rectangles). Figure has been reprinted with permission from published literature.²³⁸ © 2018 Wiley-VCH

While the intermediate coloration of the GMO blend appears the most color-neutral when holding at intermediate potentials (Figure 2.3.4), here we can see that the GMO black-to-transmissive evolution is slightly more colored than that of the CMO blend when switching in an on/off fashion between extreme potentials. Therefore, a blend similar to GMO, where the oxidation potentials are more closely aligned, would be superior for applications in which intermediate achromatic shades need to be accessed or dialed in, or when a lower driving voltage is required. On the other hand, in applications where direct black-to-transmissive transition must exhibit minimal transient coloration, a blend with components whose absorbance bands are spaced further apart, such as the CMO blend,
would be more advantageous. The broadened absorbance spectrum can compensate for disparities in the bleaching and coloration of each component.

For truly color-neutral black-to-transmissive switching, the coloration and bleaching kinetics of each chromophore should be similar so that the transition between extreme occurs through achromatic, evenly absorbing intermediate shades. However, factors that govern kinetic characteristics are complex, as they involve migration of both charge carriers and solvated ions that must occur simultaneously and, as a result, may depend on electrolyte properties and polymer microstructure. Therefore, it is difficult to predictably tune the switching kinetics through structural modifications of the polymer. In ECP blend formulations where one component bleaches at a faster rate than the others (namely, the ECP-Magenta component in the CMO and GMO blends), it appears to be advantageous if the chromophores exhibit little spectral overlap, thereby allowing for more even coverage across the visible spectrum throughout the optical transition.

3.3 Conclusion

Electrochromic technologies, such as dimmable fenestration, eyewear integrated displays, and optical shutters, require materials that reversibly transition between highly transmissive and broadly absorbing achromatic states with minimal intermediate coloration. In this work, we show how the properties of dioxythiophene-based electrochromic polymers (ECPs) can be leveraged through straightforward color mixing to yield high-contrast, black-to-transmissive materials with low driving voltages (< 1 V vs. Fc/Fe*), extended functional lifetimes, and minimal transient chromaticity.
Drawing from a family of five soluble colored-to-colorless switching polymers (including ECP-Cyan, -Green, -Magenta, -Yellow, -Orange) and following straightforward color-mixing principles, we have developed new electrochromic polymer blends that reversibly transition between highly desirable black and transmissive states. These blends include a conventional CMY subtractive combination (ECP-Cyan, -Magenta, and -Yellow), as well as CMO (ECP-Cyan, -Magenta, and Orange), and GMO (ECP-Green, -Magenta, and -Orange) formulations. Combining the constituent ECPs through scalable solution co-processing techniques allows us to control the precise ratio of the chromophores, predictably balance the chromatic contributions of each component, and access achromatic states ($C_{ab}^* < 5$) that absorb more broadly across the visible spectrum than previously reported single component donor-acceptor black-to-clear ECPs.

By incorporating different high-gap and dual-band absorbing ECPs, we demonstrate subtle control over both the extreme and intermediate coloration of the blends. Substituting the new ECP-Orange for ECP-Yellow in the CMO and GMO blends allows us to overcome the stability issues associated with the high gap component and produce blends that maintain coloration over hundreds of redox cycles without compromising electrochromic contrast. Owing to the low oxidation potential of ProDOT-rich ECP-Green, the GMO blend reaches a transmissive state at a lower potential than the CMO blend (+0.5 vs. +0.6 V), exhibits more coordinated bleaching of the constituent chromophores, and transitions through low ($a^*$, $b^*$) achromatic intermediates. Utilizing ECP-Cyan, which has an inherently broadened absorption spectrum when compared to ECP-Green, allows the CMO blend to exhibit more color-neutral on/off switching between the extreme black and transmissive states.
This work showcases how solution co-processing of ECPs can be used to access highly targeted achromatic hues while also enabling fine-tuned neutral optical transition between black and transmissive states. To achieve truly achromatic and synchronized switching of blended electrochromic materials, such as those described in this study, additional work is needed to understand the kinetic factors associate with ECP coloration and bleaching.
3.4 Supporting Figures

Supporting Figure 3.4.1 – Differential pulse voltammetry of ECP films in 0.5 M TBAPF₆/PC: A) ECP-Cyan, B) ECP-Green, C) ECP-Yellow, D) ECP-Orange, E) ECP-Magenta, F) ECP-Black. Figure has been adapted with permission from published literature. © 2018 Wiley-VCH.
Supporting Figure 3.4.2 – Differential pulse voltammetry of the various ECP black blends in 0.5 M TBAPF₆/PC: A) CMY blend, B) CMO blend, and C) GMO blend. Films were drop-cast onto glassy carbon button electrodes. Figure has been adapted with permission from published literature.© 2018 Wiley-VCH.
Supporting Figure 3.4.3 – Potential-dependent absorption spectra of A) ECP-Yellow, B) ECP-Orange, C) ECP-Cyan, D) ECP-Green, and E) ECP-Magenta in 0.5 M TBAPF$_6$/PC recorded at 0.1 V intervals. Films were prepared by spray-casting onto clean ITO/glass electrodes. Potentials reported vs. Ag/Ag$^+$. Figure has been adapted with permission from published literature.$^{238}$ © 2018 Wiley-VCH.
Supporting Figure 3.4.4 – Comparison of the neutral (0.0 V) and oxidized (+0.8 V) state spectra of A) ECP-Yellow (yellow line) and ECP-Orange (orange line), and B) ECP-Cyan (cyan line) and ECP-Green (green line). Potentials reported vs. Ag/Ag⁺. Figure has been adapted with permission from published literature. 238 © 2018 Wiley-VCH.
Supporting Figure 3.4.5 – CVs of ECP-Black and black blends performed in 0.5 M TBAPF₆/PC at a scan rate of 50 mV s⁻¹. Films were prepared by drop-casting onto glassy carbon button electrode (a = 0.07 cm²). Figure has been adapted with permission from published literature.²³⁸ © 2018 Wiley-VCH.

Supporting Figure 3.4.6 – Change in integrated absorbance (380–780 nm) as a function of pulse time for GMO (green triangles), CMY (yellow squares), and CMO (orange diamonds) when switched between -0.5 V and +0.8 V vs. Ag/Ag⁺. Figure has been adapted with permission from published literature.²³⁸ © 2018 Wiley-VCH
Supporting Figure 3.4.7 – Integrated contrast (380–780 nm) for ECP black blends recorded over 1,000 redox switches between -0.5 V and +0.8 V vs. Ag/Ag+. Spectra were obtained every 100 cycles while holding the potential at -0.5 V and +0.8 V. Figure has been adapted with permission from published literature.© 2018 Wiley-VCH.

Supporting Figure 3.4.8 – Plot of ($a^*$, $b^*$) color coordinates of ECP black blends over 1,000 redox cycles. Color coordinates were obtained every 100 cycles while holding at -0.5 V vs. Ag/Ag+. Figure has been adapted with permission from published literature.© 2018 Wiley-VCH.
Supporting Figure 3.4.9 – Spectroelectrochemistry of (A) ECP-Black, (B) CMY blend, (C) CMO blend, and (D) GMO blend. Spectra were recorded under potentiostatic conditions at 0.1 V increments ranging from -0.5 V to +0.8 V vs. Ag/Ag\textsuperscript{+} in 0.5 M TBAPF\textsubscript{6}/PC. Figure has been adapted with permission from published literature.\textsuperscript{238} © 2018 Wiley-VCH.
3.5 Additional Experimental Details

ECP-Black (Stille polymerization, $M_n = 10$ kDa; $D = 1.6$) was synthesized according to a previously published procedure by Joe Babiarz at BASF. ECP-Magenta (DHAP, $M_n = 12$ kDa, $D = 2.3$), and ECP-Cyan (DHAP, $M_n = 19$ kDa, $D = 4.3$) were synthesized using previously reported procedures. ECP-Yellow (DHAP, $M_n = 88$ kDa, $D = 3.9$) was synthesized by Michael Kuepfert at BASF using literature methods. ECP-Green (DHAP, $M_n = 68$ kDa, $D = 3.1$) were synthesized by Dr. Anna Österholm with the assistance of Dr. Chi Kin Lo. ECP-Orange (DHAP, $M_n = 25$ kDa, $D = 2.2$) was designed and synthesized by Dr. Dylan Christensen. Synthetic details for ECP-Green and ECP-Orange can be found in the literature.

For electrochemical characterization, all films were evaluated by CV and DPV using a three-electrode cell with a Pt flag as the counter electrode, an Ag/Ag$^+$ reference electrode ($E^{\frac{1}{2}}$ for Fc/Fc$^+$ couple: +65 mV), and ECP-coated glass carbon working electrode. For these electrochemical measurements, 2 µL of ECP stock solution (2 mg mL$^{-1}$ in RT toluene) was drop-casted on the glassy carbon working electrode ($a = 0.07$ cm$^2$) and allowed to dry at room temperature to form a thin film.

For optical characterization, colorimetry, and photography, all films were spray-cast from solution (as described in CHAPTER 2) from toluene solutions (4 mg mL$^{-1}$ polymer concentration) at RT.
CHAPTER 4. POLYTHIOPHENES WITH ETHYLENE GLYCOL-BASED SIDE CHAINS AS ACTIVE MATERIALS FOR AQUEOUS ORGANIC ELECTROCHEMICAL TRANSISTORS: EFFECTS OF SIDE CHAIN LENGTH AND SUBSTITUTION

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4.1 Introduction

4.1.1 Utility of OECTs

OECTs have recently gained renewed popularity due to their ability to directly transduce ionic fluxes into electronic signals. This property has enabled the development of low-voltage electronic interfaces, such as bio(chemical)-sensors and electrophysiological probes, that enable effective communication between abiotic and biotic systems. Commonly, OECTs are three-terminal electronic devices, comprising a source, drain, and gate electrode along with a redox-active CP channel active...
interfacing with an electrolyte solution. The working mechanism of an OECT involves bulk electrochemical doping of the polymer channel, where electrolyte fluxes occurring across the polymer-electrolyte interface couple are coupled to electronic charge carrier injection at the polymer-electrode interface.\textsuperscript{63,202} For a more thorough overview of the utility and operation of OECTs, the reader is directed to CHAPTER 1.3.2 and the references therein.

4.1.2 OECT Active Materials

High-performing OECT active materials support the effective transport of mixed (i.e. electronic and ionic) charges throughout the depth of the polymer channel. Variations in the gate potential are then responsible for varying the doping level of the channel and therefore the number of injected charge-balancing counter-ions in the organic semiconductor. Based on commonly espoused models, the operation of OECTs can be described by a combination of an electronic and ionic circuit,\textsuperscript{199} whereby the performance of OECTs is typically evaluated in terms of their transconductance ($g_m$), as described previously in Equation 1 in CHAPTER 1.3.2.

The two-component polymer dispersion PEDOT:PSS is perhaps the most commonly studied OECT active material (structure shown in Figure 1.3.4I). However, as explained earlier in CHAPTER 1.3.2.3, this material has some drawbacks, both in terms of its practical functionality and its limited ability to provide generalizable insight into the fundamental aspects of mixed ionic-electron conduction in conjugated polymers.
4.1.3 **EG-Functionalized CPs for OECTs**

Over the last few years, a CPs functionalized with solubilizing and polar ethylene glycol (EG)-based side chains have been studied as active channel materials for aqueous-based OECTs. Some of these materials are purported to show OECT performance that that rival or even exceed those of devices fabricated with PEDOT:PSS.\textsuperscript{194,201,203,370} Moreover, this class of materials offers numerous additional advantages compared to PEDOT:PSS, specifically due to: (i) the broad range of conjugated aromatic repeat units that can be employed to tune the transport properties of the channel,\textsuperscript{203,227,371–373} (ii) the absence of any electrically insulating polyelectrolyte component, thus enhancing the channel capacitance, (iii) the development of n-type organic semiconductors for OECTs,\textsuperscript{222,374} allowing for the fabrication of complementary circuits,\textsuperscript{111} and (iv) solubility in common organic solvents, allowing for comprehensive characterization of chemical structure, molecular weight, and purity. In EG-functionalized materials, the side chains are not only included for the purpose of solubilizing the polymer, thus rendering it compatible with solution-based processing, but the EG-based side chains also increase the overall hydrophilicity of the polymer. This is thought to facilitate the transport and stabilization of aqueous counter-ions in the CP active layer.\textsuperscript{194,228} Given the importance of these EG side chains, it is worthwhile to note that virtually every high performing p-type EG-functionalized, or “glycolated,” OECT active material employs the linear triethylene glycol motif as its side chains, with little direct comparisons evaluating the effect of side chain length distribution pattern.\textsuperscript{192,201,222,281} This is somewhat surprising, considering that modulation of the side chain length, substitution pattern, and branching point are common strategies to enhance material properties in other areas of organic electronic research.\textsuperscript{77,129,135,321,375–377}
Considering these aspects of the field, the present study evaluates the effect of both EG side chain length and substitution pattern on the aqueous redox properties and solid-state ordering of a family of polar polythiophenes. A combination of electrochemical, optical, and structural characterization techniques will help elucidate the structure-property relationships in these aqueous-compatible, glycol-functionalized polythiophenes. This family, which was based upon a high performing OECT active material reported by Nielsen et al. in 2016, demonstrates the important role of side chain structure in EG-functionalized OECT active materials.

4.2 Results and Discussion

4.2.1 Polymer Design and Preparation

Considering the aforementioned goals, a series of “glycolated” polythiophenes was designed. This family, shown in Figure 4.2.1, is based upon the a previously published high performing OECT active material. This state-of-the-art material, referred to as p(gT2-T) in its original publication, is an alternating copolymer comprised of a EG-functionalized bithiophene comonomer and an unsubstituted thiophene comonomer (Figure 4.2.1A). The overall polythiophene (PT) repeat unit consists of two thiophene rings with tri(ethylene glycol)-based side chains appended the β position. The third thiophene ring in the repeat unit is unsubstituted. In this study, this benchmark polymer is referred to as p(g3T2-T) for clarity.

In addition, this work also includes analogues of this polymer with shorter (p(g2T2-T)) and longer (p(g4T2-T), p(g6T2-T)) side chains, as shown in Figure 4.2.1A. By changing of the side chain in the p(gxT2-T) system (where x = 2, 3, 4, or 6), we maintain
the overall substitution pattern of side chain grafting onto the backbone. Two-thirds of the thiophene rings still incorporate a polar EG side chain, while one-third of the thiophene rings constitute an unmodified thiophene “spacer” without any side chains appended to it (denoted by “-T”). This is the same substitution pattern used to develop the state-of-the-art polymer p(g3T2-T). Notably, the polymer with five ethylene oxide units in the side chain ($x = 5$) was not prepared due to material limitations. However, as will be shown later, the series without this analogue is sufficient to establish relevant design rules for OECTs.

By changing the length of the side chain in the p(gxT2-T) series, we manipulate the overall relative mass fraction of the predominantly ion-conducting component (EG side chain) and hole-conducting/electroactive component (PT backbone) in the film. We represent this balance of ion- and electron-conducting material by calculating a “relative electroactive mass” percentage for each polymer (Table 4.2.1). The relative electroactive mass is given as the percentage of the theoretical total repeat unit mass comprised of the electroactive thiophene backbone. Such side chain modifications are not only expected to change the solid-state assembly and chain conformation but also drastically the ion uptake properties, redox kinetics, charge transport properties—all of which are of critical importance for designing high-performing OECT active materials.

In addition to studying the effect of side chain length, we also evaluate the role that the side chain substitution pattern has on the active material properties. This is an under-explored variable in the field of OECTs. The polymers in the p(gxT2-T) series are designed such that two out of every three thiophene rings in the repeat unit (2/3) are functionalized with EG side chains. As a comparison, we also study the polymer p(g2T2), in which every thiophene ring in the repeat unit (2/2) is functionalized with an EG side chain (Figure
Thus, the distribution pattern of the side chains is distinct, and p(g2T2) does not incorporate any unsubstituted thiophene “spacer” into the backbone.

A notable comparison can be made between p(g3T2-T), the state-of-the-art OECT active material, and p(g2T2) because these two polymers have similar electroactive masses. In other words, thin films of these materials would contain a similar percentage of electroactive polythiophene backbone relative to the total film mass (Table 4.2.1). Because both polymers share the same amount of electroactive mass, and the “capacitance” in most conjugated polymers is widely considered to be pseudocapacitive and faradaic in nature, one might expect polymers with similar relative electroactive masses to exhibit similar capacitance values. From a redox perspective, the side chains are more or less “dead weight” that do not inherently contribute to the electronic properties of the material. In fact, removal of side chain density has previously been leveraged as a strategy for enhancing the mass capacitance of conjugated polymers. However, when side chains are necessary to impart solubility of a CP, polar side chains are advantageous for supporting the uptake of a surrounding aqueous electrolyte. Modification of side chain substitution pattern may also influence the extent of inter- and intra-chain interactions that play a role in charge carrier stabilization and transport. This, in turn, would hypothetically impact redox and charge storage properties.
Figure 4.2.1 – Repeat unit chemical structures of EG-functionalized PTs to be explored as potential aqueous-compatible CPs for OECT applications, showing A) polymer series with varying side chain length but similar substitution pattern, and B) polymer pair with differing substitution pattern but similar electroactive mass.

In addition to having a different side chain substitution pattern, the polymer p(g2T2) is also expected to be more electron rich than the p(gxT2-T) family due to the increased π-donation from the substituent oxygens. This is also expected to influence the redox properties by lowering the oxidation onset and perhaps also stabilizing holes along
the backbone. As will be demonstrated, the interplay of these steric, electronic, and intermolecular interactions results in very different properties across the polymer family.

The polymers were synthesized via step-growth Stille polycondensation reactions by Dr. James Ponder and Maximilian Moser, collaborators at ICL working under Prof. Iain McCulloch. Prior to beginning this work, the structure and composition of the materials was confirmed by NMR. Details concerning the polymer synthesis and chemical characterization can be found in the published literature. Due to unique experimental restrictions, elemental analysis was not performed.

GPC was used to provide an estimate the approximate macromolecular weight. While the molecular weight by GPC is only an approximate measure of weight, as it is benchmarked against a standard and relies on assumptions regarding hydrodynamic radii, it is a generally accepted method for comparing the relative sizes polymers with similar chemical structures. As shown in Table 4.2.1, the GPC-determined $M_n$ of these materials range between 10-30 kDa, which is a rather narrow window in regards to the range of $M_n$ for conjugated polymers reported in the literature. These weights are higher than some of the common OECT active materials reported in the literature, some of which have reported $M_n$ values below 10 kDa. While the influence of molecular weight on OECT performance has not yet been systematically studied, many properties of conjugated polymers (mobility, microstructure, thermal properties, mechanics) often show a degree of dependence on molecular weight up until some critical degree of polymerization ($X_n$) is reached. In rr-P3HT, molecular weight has been shown to appreciably influence the redox properties and absorption signatures of the polymer until an $M_n$ of ~9 kDa. On this basis, this study generally assumes that the differences in molecular weight among the
polymers are not sufficiently significant to be the governing factor in the property differences. Future studies should be aimed at systematically investigating absolute molecular weight effects (not GPC-estimated molecular weight), especially as it relates to mixed conduction properties and the associated OECT performance.

Table 4.2.1 – General polymer properties of polar PTs prepared for this study, including molecular weight information and relative electroactive mass values.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kDa)$^a$</th>
<th>Đ</th>
<th>Relative Electroactive Mass$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(g2T2-T)</td>
<td>11</td>
<td>1.3</td>
<td>50%</td>
</tr>
<tr>
<td>p(g3T2-T)</td>
<td>23</td>
<td>2.0</td>
<td>43%</td>
</tr>
<tr>
<td>p(g4T2-T)</td>
<td>28</td>
<td>2.5</td>
<td>37%</td>
</tr>
<tr>
<td>p(g6T2-T)</td>
<td>13</td>
<td>2.1</td>
<td>29%</td>
</tr>
<tr>
<td>p(g2T)</td>
<td>21</td>
<td>3.4</td>
<td>41%</td>
</tr>
</tbody>
</table>

$^a$ Molecular weight determined by CHCl$_3$ GPC (40 °C) vs. PS standards.
$^b$ Corresponds to theoretical mass percentage of polythiophene backbone relative to total theoretical repeat unit mass, including backbone and side chains.

Due to the significant variation in the side chain length of the polymers, the polymers displayed markedly different solubilities. For instance, p(g2T2-T) exhibited low (<1 mg mL$^{-1}$) solubility in RT chloroform. Polymers p(g3T2-T) and p(g4T2-T) were readily soluble (up to ~25 mg/mL) in chloroform. As anticipated, the polymer with the longest side chains, p(g6T2-T), was soluble in a range of solvents including chloroform,
ethyl acetate, acetone, and methanol. Chloroform was chosen as a processing solvent for all polymers, except for p(g2T2-T), which needed to be processed from a warm (50 °C) chloroform/chlorobenzene mixture.

4.2.2 Electrochemical Properties

4.2.2.1 Basic Voltammetric Characterization

The electrochemical properties of the solution-processed polymer films were evaluated by differential pulse voltammetry (DPV) and cyclic voltammetry (CV) in a degassed 0.1 M NaCl/H₂O electrolyte. Details regarding electrochemical analysis are reported in Table 4.2.2. DPV was employed to determine the onsets of oxidation (E_{ox}) of each material. The DPV traces recorded for each polymer can be found in Supporting Figure 4.4.1. Each polymer showed an E_{ox} around -0.2 V vs. Ag/AgCl with a variation of ±0.1 V across the polymer series (Table 4.2.2).

The aqueous CV traces are shown in Figure 4.2.2A. Each of the five polymers can be oxidized and reduced repeatedly in water, as evidenced by the anodic and cathodic waves observed in the CV. Each of the polymers studied also displayed two distinct oxidation waves within the electrochemical window of water. Typically, the first anodic wave in the CV is attributed to the oxidation of “aggregated” or “crystalline” polythiophene domains, while subsequent oxidations are thought to correspond to the oxidation of disordered or “amorphous” regions of the film.

First, we will compare the redox properties of p(g2T2) and p(g3T2-T), which differ in their side chain distribution pattern but maintain similar electroactive masses and
hydrophobic-hydrophilic balances. The polymer p(g2T2) has the first lowest $E_{ox}$ (-0.27 V) of all materials tested, but only by a small difference. Despite having more electron-donating substituents, the $E_{ox}$ of p(g2T2) was very close to that of p(g3T2-T) (-0.27 V vs. -0.25 V). This could be explained by several possible phenomena. First, the incorporation of the unsubstituted thiophene “spacer” unit in the p(g3T2-T) could improve the intermolecular ordering of films (increased aggregation, better $\pi$ stacking, and/or less steric hindrance to planarization) that result in improved $\pi$ orbital overlap and a lower ionization potential. Secondly, this unsubstituted thiophene could allow for the side chains to adopt a more “ideal” conformation for $\pi$ orbital lap between the adjacent oxygen and the thiophene ring, thereby promoting more electron donation into the PT backbone. In the latter case, the electron densities in both backbones may be comparable, which would explain the similarity in the first $E_{ox}$.

While p(g3T2-T) shows a broad capacitive-like plateau after +0.1 V, p(g2T2) does not show such a capacitive current profile. Also, a minimal amount of current is passed with the first oxidation wave of p(g2T2) ($E_{ox}$ #1 = -0.27 V), while most current is passed with the second oxidation process ($E_{ox}$ #2 = +0.02 V). Because these two processes are thought to be related to electronically resolvable subpopulations with different extents of order, this result suggests that the p(g2T2) has a lower fraction of ordering/aggregated components relative to p(g3T2-T). As there is no precedent for quantifying these subpopulations based on CV, this conclusion remains highly speculative. If true, this result would indicate that functionalization of every thiophene ring with a side chain suppresses ordering of the polymer. As will be shown later, complementary methods (which probe other aspects of order) will be used to qualitatively support this claim.
Table 4.2.2 – Oxidation onsets of EG-functionalized PTs in aq. NaCl.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{ox}}$ #1 (V)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$E_{\text{ox}}$ #2 (V)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(g2T2-T)</td>
<td>-0.10</td>
<td>+0.15</td>
</tr>
<tr>
<td>p(g3T2-T)</td>
<td>-0.25</td>
<td>+0.11</td>
</tr>
<tr>
<td>p(g4T2-T)</td>
<td>-0.14</td>
<td>+0.08</td>
</tr>
<tr>
<td>p(g6T2-T)</td>
<td>-0.10</td>
<td>+0.21</td>
</tr>
<tr>
<td>p(g2T2)</td>
<td>-0.27</td>
<td>+0.02</td>
</tr>
</tbody>
</table>

Potentials reported vs. Ag/AgCl reference (3 M NaCl/H<sub>2</sub>O inner solution).

<sup>a</sup> Determined by DPV performed on drop-cast films in degassed 0.1 M NaCl/H<sub>2</sub>O.

<sup>b</sup> Determined by EIS on blade-coated films on ITO/glass in degassed, as described previously. Uncertainties represent standard deviation of 3+ films, cast and measured separately.

Next, we turn our attention to the effect of side chain length by comparing the CVs of the p(gxT2-T) presented in Figure 4.2.2. Relative to the state-of-the-art polymer, p(g3T2-T), increasing or decreasing the length of the EG side chains decreased the current density upon doping. In fact, the overall current in the CV decreases in the following order p(g3T2-T) > p(g4T2-T) > p(g2T2-T) ≈ p(g6T2-T), as evident from Figure 4.2.2A. This finding was unexpected, considering that the electroactive masses of the polymers, i.e. the mass percentage of conjugated backbone relative to the whole polymer, were 50%, 43%, 37% and 29% for p(g2T2-T), p(g3T2-T), p(g4T2-T) and p(g6T2-T) respectively (Table 4.2.1). With the greatest relative electroactive mass, polymer p(g2T2-T) was thus expected to be able to pass the highest amount of charge across one electrochemical doping/de-doping cycle.
One possible reason for polymer p(g2T2-T)’s reduced ability to store electronic charges is due to its short EG chains, which may render the material less permeable to charge compensating counter-ions. Moreover, the shorter EG chains are also likely to stabilize the negatively charged hydrated counter-ions to a lesser degree. However, we will observe through spectroelectrochemistry studies in CHAPTER 4.2.3, p(g2T2-T) is able to fully dope within the electrochemical window of water—thus proving that ion penetration is not causing the low current density of p(g2T2-T). Therefore, we hypothesize the low current density of p(g2T2-T) is due to other factors, which will be discussed later.

The EG side chain length in p(g3T2-T) seemed to be an ideal length, enabling this material to pass the highest amount of charge in one electrochemical cycle across the polymer series. Polymers with intermediate side chain lengths, p(g3T2-T) and p(g4T2-T), appear to pass the greatest current with the most significant capacitive charging, as indicated by the large current plateau beyond +0.3 V (Figure 4.2.2). Further increasing the side chain length in p(g6T2-T) leads to a decrease in current density. While this result is in part due to the decreased electroactive mass of p(g6T2-T), the low current density in p(g6T2-T) predominantly arises from dissolution and/or dispersion of the doped polymer in the aqueous electrolyte. Consequently, these results indicate that a strategic balance in the EG length must be achieved during the design of EG functionalized conjugated polymers for OECTs. The chosen EG side chain length must be sufficiently long to allow for electrochemical charging of PT backbone without rendering the polymer so polar that it disperses in the electrolyte upon doping.
Figure 4.2.2 – A) Cyclic voltammograms of EG-functionalized polythiophene drop-cast films on glassy carbon button electrodes, performed at 50 mV s⁻¹ in degassed 0.1 M aqueous NaCl. B-F) Scan rate dependence of CV peak current density for each polymer. Points connected with solid lines represent experimental data. Dashed line represents the linear projection of \( i_p \) density, as determined by data within non-diffusion limited regimes (\( \nu \leq 50 \text{ mV s}^{-1} \)) and fit to a linear regression. Figures have been adapted with permission from the literature and modified (additional data added). © 2020 American Chemical Society.
To evaluate the speed of the electrochemical doping/de-doping process, the peak current density \(i_p\) in the CV was studied as a function of scan rate \(v\) (Figure 4.2B-F above). When the electron charge transfer resistance within the film and between the underlying film and the electrode is assumed to be negligible, this experiment allows us to evaluate the ion diffusion limitations associated with the redox process. For thin films adsorbed to electrodes (i.e. “modified electrodes”), \(i_p\) is directly proportional to \(v\). When redox processes become diffusion-controlled, the \(i_p\) vs. \(v\) relation deviates from linearity and adopts a square root dependence with \(i_p\) proportional to \(v^{1/2}\).

As shown in Figure 4.2.2, the length of the side chain plays a role in the CV scan rate dependence. Polymers \(p(g2T2-T)\), \(p(g3T2-T)\) and \(p(g4T2-T)\) all exhibited relatively linear dependencies of the peak current density on the scan rate up to at least \(v = 500 \text{ mV s}^{-1}\), thus facilitating rapid charging and discharging, which is favorable in the context of recording short-lived biological signals with OECTs. Interestingly, despite having longer ion-transporting side chains, \(p(g4T2-T)\) becomes noticeably diffusion-limited at slower scan rates than \(p(g3T2-T)\) (\(v = 500 \text{ mV s}^{-1}\) vs. \(v = 100 \text{ mV s}^{-1}\)). This suggests that polar side chains can only promote aqueous redox activity to a limited extent. Beyond an optimal side chain length, long polar substituents actually begin to encumber the redox process. One potential limitation to this measurement lies in the potential window used for the experiments (-0.5 to +0.8 V vs. Ag/AgCl), which corresponds to slightly different overpotentials and therefore may change the current response slightly, as explained in CHAPTER 2.3.1. However, the differences in overpotential here are rather small (within 0.1 V), thus we assume the effect of the overpotential is negligible.
At low scan rates (ν = 5 mV s⁻¹), the polymer with the shortest side chains p(g2T2-T) exhibits current densities that are comparable with the other materials. At higher scan rates, the current passed by p(g2T2-T) diminishes relative to the rest, despite maintaining a linear scan rate dependence. Therefore, while charge diffusion in the film is not more limited in p(gT2-T), the lower slope of the i_p vs. ν curve suggests that the polymer either (i) has a lower overall concentration of accessible redox sites in the film, or (ii) that the redox sites in the film experience repulsive interactions. Such observation could also potentially explain the low current density and charge storage capacity for this material. Without further experimentation, we cannot definitively comment on whether explanation (i) or (ii) is the dominant factor governing the current response of p(g2T2-T). The lack of elemental analyses prevents us from confidently excluding explanation (i), seeing as we can make no indubitable statement about potential impurities that would lower the redox site density. Simultaneously, explanation (ii) seems plausible, as the polymer with the shortest EG side chains may be more rigid, which could potentially prevent conformational re-organization to stabilize high charge densities along the backbone.

Compared to the other polymers, p(g6T2-T) was maintained linear dependence of i_p up to ν ≈ 200 mV s⁻¹. Further increases in the scan rate for p(g6T2-T) resulted in a partial delamination and dispersion or dissolution of the polymer in the electrolyte. Representative CV traces for polymer (g6T2-2) conducted at a range of scan rates are shown in Supporting Figure 4.4.2A. This plot shows the tenth cycle from each set of ten CVs performed at each scan rate. The initial CV scans conducted at ν = 50 mV s⁻¹ were performed to condition the film, as explained in CHAPTER 2.3.1. Considering the dispersion/partial dissolution we
observed of the film in the electrolyte, we interpret this loss in current density to be the result of poor polymer adhesion to the underlying glassy carbon electrode.

To better compare the shapes of the CV traces for each scan rate, we have normalized the current data and presented it in Supporting Figure 4.4.2B. As can be seen from the plot, the initial “conditioning” scan performed at 50 mV s\(^{-1}\) shows a similar shape to the subsequent CV performed at 5 mV s\(^{-1}\), with \(i_p\) occurring at +0.4 V. With additional scans at faster scan rates (10, 25, and 50 mV s\(^{-1}\)) the CV traces show a shifting of \(i_p\) to higher voltages. The drastic difference between the initial “conditioning” scan at 50 mV s\(^{-1}\) and the later 50 mV s\(^{-1}\) scan is consistent with the observed dispersion of the polymer in the electrolyte. The similarities between the initial cycles at 50 mV s\(^{-1}\) and the subsequent cycles at 5 mV s\(^{-1}\) suggests that polymer adhesion to the electrode, and not necessarily poor electron transfer kinetics or diffusional/mass transfer limitations, is responsible for the sub-linear scan rate dependent CV characteristics. Considering the physical instability of this material in the aqueous electrolyte, it is difficult to draw any conclusion regarding transport properties solely from whether the different CV trace shape recorded for p(g6T2-T). In sum, the long EG side chains in p(g6T2-T) render the polymer exceedingly polar.

In addition to the side chain length, the side chain substitution pattern also changes the scan rate dependence of the doping/de-doping reaction. Polymers p(g3T2-T) and p(g2T2), which have similar electroactive masses but are differently substituted, exhibit distinct scan rate dependence (Figure 4.2.2B, E). The polymer with the unsubstituted thiophene and longer side chains, p(g3T2-T), shows fast charging/discharging and less diffusion-limited behavior. One possibility for this is the longer side chains in p(g3T2-T) vs p(g2T2.). However, we know from the comparison of p(g3T2-T) and p(g4T2-T) that
longer side chains do not necessarily always result in faster charge transport the film. Instead, there may be differences in chain conformation and microstructure that better facilitate diffusion in p(g3T2-T) relative to p(g2T2). Seeing that p(g2T2), despite having a similar E_{ox} to that of p(g2T2-T), passes most of its current at higher potentials, it is also possible that the overpotential variations might govern the rate-dependent current response for these two materials. Further studies are needed to explore these potential differences and establish firm explanations for their origin.

4.2.2.2 Capacitance

As described previously, the volumetric capacitance (C*) of a conjugated polymer is proposed to be an important metric for OECT device performance.\textsuperscript{175,201,381} Accordingly, EIS was used to calculate the potential-dependent C* of the materials. Because polymer p(g6T2-T) delaminated from the electrode upon repeat cycling, this material was excluded from EIS studies. Because determination of C* relies on normalization to film volume, which in turn requires a well-defined film thickness, blade-coating was used to fabricate uniform, rectangular films (except for pg2T2-T, which was spray-coated due to poor solubility). For more information about C* and the EIS methods used in this study, the reader is directed to CHAPTER 1.3.2, CHAPTER 2.3, and the references therein.

The results of the potential-dependent C* calculations are shown in Figure 4.2.3. Generally, the evolution of C* as a function of potential tracks with the current density in the cyclic voltammograms, as expected. The state-of-the-art OECT active material p(g3T2-T) shows a high peak C* (210 ± 19 F cm\textsuperscript{-3} at +0.2 V), which is consistent with values reported for this material in the literature (220 ± 30 F cm\textsuperscript{-3}).\textsuperscript{203} Polymers with shorter and
longer side chains, p(g2T2-T) and p(g4T2-T), yielded lower peak C* values of 8 ± 2 and 192 ± 10 F cm⁻³, respectively. In the case of p(g2T2-T), the markedly low C* was consistent with the low current density observed in the CV (Figure 4.2.2A). As discussed earlier, while we are unable to definitively identify the cause of this low current density, we speculate it is related to a lower redox site density, repulsive interactions between redox sites, and/or the inability of the material to undergo a conformational rearrangement to stabilize excess charges. Combined with its low solubility, the relatively poor redox properties of p(g2T2-T) make it an undesirable active material for aqueous OECTs.

On the other hand, the longer side chain length of p(g4T2-T), did not contribute to additional ion stabilization, thus only leading to a decrease in the proportion of electroactive mass of the polymer, consequently leading to a reduced C*. It is worthwhile to note that normalization the C* values obtained for p(g3T2-T) and p(g4T2-T) by the relative percentages of electroactive mass present in each polymer, i.e. 43% and 37% respectively, affords similar electroactive normalized volumetric capacitances around 490 F cm⁻³. Therefore, differences in the capacitance of these materials appear to scale roughly with the relative electroactive fractions of these two polymers. We posit that the observed capacitance differences for p(g3T2-T) and p(g4T2-T) can be attributed to their respective electroactive masses, and not any intrinsic differences in the formation and stabilization of charges in these materials. Accordingly, we expect that any elongation in the side chain beyond the length used p(g4T2-T) would result in a similar reduction in C*. 
Figure 4.2.3 – Volumetric capacitance ($C^*$) of blade-coated polythiophene films determined by EIS in 0.1 M NaCl/H$_2$O. Error bars represent standard deviations of measurements performed on 3+ different films, cast and measured separately. Figures have been adapted with permission with permission from the literature$^{368}$ and modified (additional data added). © 2020 American Chemical Society.

A perhaps more interesting observation can be made by comparing polymers $p(g3T2-T)$ and $p(g2T2)$, which have similar relative electroactive masses (43% vs. 41%) but a fundamentally different side chain substitution pattern. Overall, the $C^*$ of $p(g2T2)$ is markedly lower than $p(g3T2-T)$, and it peaks at a much higher potential ($156 \pm 15$ F cm$^{-3}$ at +0.40 V, Figure 4.2.3). Even when evaluating $p(g2T2)$ against $p(g4T2-T)$, which has substantially lower relative electroactive mass (37%), the $C^*$ of $p(g4T2-T)$ is still nearly 25% greater than that of $p(g2T2-T)$. Consequently, it seems that substituting every repeat unit with a polar side chain reduces the overall capacitance of the material. When targeting high $C^*$, it is much more advantageous to incorporate unsubstituted aromatic units into the
backbone and then lengthen the polar side chains for sufficient solubility, rather than functionalize more aromatic units with a smaller side chain. This design strategy appears to increase the concentration of faradaic charges in the film.

Because these capacitance measurements are normalized to film volume, observed differences in C* could alternatively possibly be explained by differences in polymer film density. For a constant film volume, a denser (more crystalline) polymer would have a higher effective mass fraction of redox-active material, thus inflating the C*. However, qualitative assessment of the CVs (Figure 4.2.2A), which are normalized both for electrode area and polymer mass, clearly show that the approximate dynamic redox capacity by CV shows the same trend as the steady state C* by EIS. Polymer p(g3T2-T) appears to pass the highest charge over the tested voltage window, followed by p(g4T2-T), p(g2T2), and p(g2T2-T) (Figure 4.2.2A). Thus, we can see from these i-V characteristics that the higher capacitance of p(g3T2-T) is not the result of differences in sheer physical density because a similar trend is observed when comparing mass-normalized data. Therefore, we conclude that the C* trends reflect a fundamental material property. The side chain substitution pattern in p(g3T2-T) results in an overall enhanced capacitance, whether it be volumetric or gravimetric.

4.2.2.3 Redox Stability

Cyclic voltammetry was also employed as a preliminary tool to study the redox stability of the polymers. Each polymer was subjected to 100 full doping/de-doping cycles across a potential range from -0.5 V to +0.8 V vs. Ag/AgCl in an aqueous 0.1 M NaCl supporting electrolyte. This test roughly simulates the conditions encountered during
repeat OECT device operation. The CV traces were integrated to give the charge passed by each CV cycle (Figure 4.2.4A-B). In addition to these repeat doping/de-doping experiments, CVs were also recorded before and after performing the potentiostatic EIS measurements used for C* calculations (Figure 4.2.4C-D). This experiment would simulate a situation where the OECT spends extensive time in a steady “on” state where the polymer is held at p-doping potentials. Note that CVs presented in Figure 4.2.4C-D differ from the CV traces in Figure 4.2.2A due to variations in casting procedure. As explained earlier in CHAPTER 2.3.1 (pp. 68), variations in drop-casting on small button electrodes can result in the peaks seen in Figure 4.2.2A, while the CVs in Figure 4.2.4C-D represent films coated only on a planar conducting ITO surface.

When monitoring the stability of the materials, electrochemical measurements are chosen over optical methods (e.g. UV-Vis-NIR absorption spectroscopy) for two reasons. First, in the context of OECT devices, the electrochemical properties are more directly associated with the desired functionality of the active material. Secondly, changes in the optical properties of the polymer upon repeat doping/de-doping, while certainly interesting, do not necessarily relate to electrochemical functionality. For instance, changes in polymer conformation or aggregation may result in evolution of the material’s absorbance line shape or oscillator strength, which are not predictably related to redox properties in a straightforward manner.

As shown in Figure 4.2.4A, all polymers undergo a noticeable loss in charge retention upon repeat cycling the aqueous electrolyte, even when studied under inert conditions. Except for p(g6T2-T), which was observed to physically delaminate and disperse in the supporting electrolyte upon doping, we hypothesize that this loss in current
is due to electrochemical degradation of the polymer films. For polymers \(p(g^2T^2)\), \(p(g^3T^2)\) and \(p(g^4T^2)\), which share the same substitution pattern, approximately 95% of charge was maintained after 100 cycles. These materials show greater stability than the polymer \(p(g^2T^2)\), which does not have any unsubstituted thiophene rings (Figure 4.2.4B).

A similar trend is observed when comparing the charge retention of \(p(g^3T^2)\) and \(p(g^2T^2)\) before and after performing EIS, where the CV of \(p(g^2T^2)\) loses considerably more charge than \(p(g^3T^2)\) and adopts a considerably different CV shape after EIS (Figure 4.2.4C, D).

![Figure 4.2.4](image)

**Figure 4.2.4** – A) Charge retention of PT films reported as a percent relative to charge passed in 10th CV cycle. B) First 100 CVs for \(p(g^2T^2)\). C-D) CV of film blade-coated films on ITO/glass before and after EIS studies. Panel A has been adapted with permission with permission from the literature. © 2020 American Chemical Society.
The proposed electrochemical degradation mechanisms of PT and other polyheterocycles (e.g. PPy) involve nucleophilic addition (by water, chloride, hydroxide, etc.) at the unsubstituted and sterically unprotected β position of the thiophene ring. This is thought to be accompanied by proton loss, tautomerization, a loss of conjugation, and/or other side reactions. With this in mind, one may expect the polymers with the unsubstituted thiophenes p(gxT2-T) to be more susceptible to degradation than p(g2T2), which has fewer of these vulnerable “open” β positions. Contrary to this thought, p(g3T2-T) and p(g4T2-T) actually show greater stability than p(g2T2). In fact, p(g3T2-T) maintains 90% of its charge density up to 1000 redox cycles (Supporting Figure 4.4.3).

We entertain several possible explanations for this observation. One possible explanation for this is that the longer side chains in these polymers keep nucleophiles further away from the backbone. However, polymer p(g2T2-T), which also has short side chains, does not suffer from poor stability like p(g2T2), therefore excluding this possibility.

Another potential explanation for the stability trend could lie in differences in the redox states of the polymers when cycling between -0.5 to +0.8 V. With an electron-donating oxygen substituent on every thiophene ring, p(g2T2) is the most electron rich and therefore has the lowest $E_{ox}$ #1 at -0.27 V (Table 4.2.2). Therefore, it may be expected for this polymer to be the most charged +0.8 V, which could potentially contribute to increased reactivity and degradation. However, we also note that most of the current passed in the oxidation of p(g2T2) occurs at higher potentials (above +0.4 V) and after the second oxidation onset, $E_{ox}$ #2. Therefore, the overpotential relative to the $E_{ox}$ #1 is not really a good indicator of oxidation state when there are multiple redox processes contributing to the doping process. Also, as we will see later, there is no spectral evidence supporting the
notion that the polymers are in vastly different oxidation states at +0.8 V. Accordingly, this theory is also excluded.

The differences in stability observed for p(g2T2) and the p(gxT2-T) may also arise from possible differences in microstructure and/or chain conformation induced by the unique side chain substitution patterns. More ordered polymers with may resist degradation, as charge carriers are stabilized and less reactive. In addition, more aggregated or crystalline polymer domains may impede infiltration of excess reactive species into the film, thereby blocking reactions with the π-conjugated backbone and slowing degradation rates. This would be similar to findings established for photodegradation pathways of CPs, where films with extended regions of conjugation, increased crystallinity, and tightly packed side chains resist the transport of reactive exogeneous species into the film.\textsuperscript{312,383–385} Microstructural differences may result in different extents of swelling, therefore introducing varying extents of potential nucleophiles (such as water) in the film, which could change the stability of the materials.

Finally, we also consider that the potential range used in these experiments may result in unexpected differences in stability. By using an aqueous electrolyte, the electrochemical cycling tests were limited by the stability window of water. Previous work has shown that degradation induced by attack of the β positions tends to occur at potentials that are slightly outside this window.\textsuperscript{382} Seeing as the polymer structure, film preparation method, and experimental conditions for these early studies are slightly different than those used in this work, we cannot assume that the degradation process occurs at exactly the same potential. Nonetheless, this observation does open the possibility that the relatively small potential window used in these experiments mitigated degradation by β-substitution.
Within the potential window used, perhaps degradation is driven by some other process that is not as well understood.

4.2.3 Optical Properties

To further characterize the properties of these materials, the linear absorption of the films was recorded as a function of the applied electrochemical potential. Polymers were cast on ITO/glass via blade coating (except for p(g2T2-T), which was spray-cast due to poor solubility) and configured into a three-electrode cell. Note that the high background for the p(g2T2-T) spectra (Figure 4.2.6A) is due to scattering from the polymer film’s rough surface, which arose from spray-casting this material from an aggregated solution. All as-cast spectra (pristine films at V_{oc}) show some degree of absorbance in the NIR (~800-1200 nm). This is indicative of the presence of charge carriers and suggests that the pristine films are partially doped under ambient conditions (Figure 4.2.6). The polymer films were subjected to 10 CV cycles as an electrochemical conditioning step. After conditioning, a -0.5 V bias was applied, which was intended to fully de-dope the polymer films.

First, we will focus on the absorption spectra of the polymer films immersed in the aqueous electrolyte and biased at -0.5 V. At this cathodic potential, the polymers should be in their de-doped (neutral) state based on the DPV data. Accordingly, the UV-Vis-NIR absorption spectra should be dominated by the π-π* transition of the neutral exciton (~600 nm). When comparing the absorption spectra of each film (Figure 4.2.5), it is clear that while the overall spectra of the polymers are somewhat similar, there are subtle differences in their line shape and energies. We note that the residual slight residual absorbance band
in the NIR for p(g2T2-T) is due to “trapped” positive charges that are not able to be extracted by the applied potential.

Figure 4.2.5 – F) Superimposed absorption spectra of each polymer film held at -0.5 V in 0.1 M NaCl/H2O. Discontinuities in absorbance at ~800 nm (indicated by gray dashed arrow) are an artifact associated with changing the spectrophotometer diffraction grating. The figure has been adapted with permission with permission from the literature and modified. © 2020 American Chemical Society.

Figure 4.2.5 allows for a comparison to be made between the absorption spectra of p(g2T2), which has a side chain on every thiophene ring of the backbone, and that of the p(gxT2-T) series, which have side chains on 2/3 of the thiophene rings in the backbone. This comparison sheds light on the influence of side chain substitution pattern on the optical properties of the material, which can be diagnostic of chain conformation and intermolecular ordering. The absorption spectrum of p(g2T2) at -0.5 V is relatively broad
and featureless, as shown by the red trace in Figure 4.2.6. This polymer also shows the most blue-shifted wavelength of maximum absorbance ($\lambda_{\text{max}} = 582$ nm) and highest energy optical gap ($E_g = 1.65$ eV). Meanwhile, the absorption spectra of most of the $p(g_xT2\cdot T)$ series (which were synthesized with a fundamentally different side chain substitution pattern) do show some evidence of vibronic coupling in their absorbance spectra (especially for polymers where $x = 2, 3, \text{and } 4$). Moreover, the $\lambda_{\text{max}}$ and $E_g$ values of the $p(g_xT2\cdot T)$ series are considerably red shifted (Table 4.2.3). The absorbance energy, breadth, and line shape of $\pi-\pi^*$ transitions depend on a host of interrelated factors, such as $\pi$ electron density, frontier orbital configuration, chain conformation, homogeneous and inhomogeneous broadening, and the relative contributions of intra- and inter-molecular aggregation. In particular, the effects of aggregation on the absorbance line shape of polythiophenes been extensively studied by Spano, Silva, Clark, and co-workers, who have developed quantitative descriptions relating the relative intensity of the vibronic features in polythiophenes to balance of HJ aggregation and extent of exciton delocalization.\textsuperscript{386–389} Kohler and co-workers have also contributed significantly to interpreting the absorbance spectra of polythiophenes with different extents of ordering.\textsuperscript{390–392} In the context of these models, the blue-shifted and unstructured absorbance spectra of $p(g2T2)$ is indicative of reduced molecular aggregation. In a situation where all polymers adopted a similarly uncoupled conformation, one might expect $p(g2T2)$ to show the most red-shifted absorbance based on the additional oxygen functionalization, which adds $\pi$ electron density in the backbone (thus destabilizing the HOMO) and promotes S-O interactions thought to planarize the chains.\textsuperscript{83} However, the trend result is observed, and $p(g2T2)$ has the highest energy and least structured absorption spectrum.
This observation suggests that functionalization of every repeat unit with a side chain hinders intermolecular interactions that promote aggregation. Meanwhile, incorporating an unsubstituted thiophene ring into the backbone facilitates aggregation – even when the length of the side chain is increased (as in p(g3T3-T)) or even doubled (as in p(g4T2-T). In the context of both the optical and the electrochemical properties, we observe signatures that suggest a reduction in qualitative, molecular level “order” or “aggregation.” In p(g2T2), such signatures are associated with a reduced volumetric and gravimetric capacitance, even when E_{ox} is not adjusted much. This result suggests that enhancing aggregation may be an important strategy for enhancing C* in OECT active materials. The substitution pattern utilized in the p(gxT2-T) series appears to be beneficial for inducing these desirable properties.

Table 4.2.3 – Optical properties from the absorption spectra of glycolated PT films in 0.1 M NaCl at biased at -0.5 V vs. Ag/AgCl.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ_{max} (nm)</th>
<th>E_{opt} (eV)(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(g2T2-T)(^{b})</td>
<td>615</td>
<td>~1.66</td>
</tr>
<tr>
<td>p(g3T2-T)</td>
<td>604</td>
<td>1.66</td>
</tr>
<tr>
<td>p(g4T2-T)</td>
<td>611</td>
<td>1.65</td>
</tr>
<tr>
<td>p(g6T2-T)</td>
<td>600</td>
<td>1.69</td>
</tr>
<tr>
<td>p(g2T2)(^{b})</td>
<td>582</td>
<td>1.70</td>
</tr>
</tbody>
</table>

\(^{a}\)E_{opt} extracted from the low-energy onset of visible light absorption.

\(^{b}\)Film is a not in fully de-doped state at this potential, thus limiting the accuracy of the extraction of E_{opt}. 

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Within the p(gxT2-T) series, one can also evaluate the effect of side chain length on the optical properties of the material. As tabulated in Table 4.2.3, $\lambda_{\text{max}}$ of the series ranges from 600-615 nm, while $E_{\text{opt}}$ all fall around ~1.70 eV. The polymers featuring shorter EG side chain lengths, p(g2T2-T), p(g3T2-T) and p(g4T2-T), all featured a structured $\pi$-$\pi^*$ absorption band with a prominent contribution from a low-energy shoulder that we attribute to the 0-0 vibronic transition ($A_{0,0}$). In the context of the descriptions developed by Spano and Silva, the moderate suppression of the $A_{0,0}$ is consistent with polymers that adopt predominantly H-type aggregates such as P3HT, with the relative ratio of the two principal vibronic features ($A_{0,0}/A_{0,1}$) being directly related to an enhanced contribution of intrachain (J-like) coupling, longer conjugation lengths, increased exciton delocalization, and overall a higher percentage of aggregates in the film. In p(g6T2-T), there does appear to perhaps be some vibronic structure buried in the spectra, but it is rather weak and seems to show a slightly lower $A_{0,0}/A_{0,1}$, which in P3HT is associated with reduced exciton delocalization. This may be evidence of reduced chromophore aggregation related to the markedly long “g6” side chains with six ethylene oxide units.

Meanwhile, the absorption spectrum of de-doped p(g3T2-T) is extremely bizarre and broad, especially as it extends into the low-energy region (Figure 4.2.5, blue trace). This broad absorbance profile was observed repeatedly when testing films of different optical densities. This spectrum is considerably broadened even when compared to the spectrum of a different batch of the identical polymer reported in the literature. The broadening observed for this batch of p(g3T2-T) would suggest an increased contribution from species with shorter effective conjugated lengths, i.e. “non-aggregated” chains.
Presently, it is unclear why the polymer absorbs in this fashion, especially seeing as its $M_n$ and $D$ are not remarkable compared to the rest of the polymers studied (Table 4.2.1).

While the above discussion surrounded the spectra of the polymer films at a single potential (-0.5 V), we now evaluate the spectra as a function of potential to study the electrochemical doping process. As evident in Figure 4.2.6, the materials exhibit similar electrochromic responses in aqueous NaCl. Each of the as-cast films required the application of a negative potential to further de-dope the film. Application of an increasingly positive potential up to +0.5 V led to a reduction of the $\pi-\pi^*$ absorption centered around 600 nm, with the concomitant appearance of absorption features at longer wavelengths peaking around 900 nm and further into the NIR (>1300 nm), which is attributed to polaronic and bipolaronic forms of the doped polymer.

For polymers p(g3T2-T) and p(g4T2-T) (Figure 4.2.6B,C), the formation of the polaronic band around 900 nm appear to be mediated by an early absorbance at ~1100 nm that grows within the first stages of doping. Notably, this distinct feature is absent in the spectroelectrochemical studies of p(g2T2) (Figure 4.2.6E), where the NIR absorption increases relatively uniformly across 800-1100 nm during the initial stages of doping. The factors governing the evolution and shape of the polaron band are not yet well-understood, and the origin and identity of this state will not be the subject of this work. Some studies have suggested these early red-shifted polaron features are indicative of distinct types of charges forming in ordered regions (called “zones of different crystallinity” by Szkurlat et al.)\(^\text{394}\) If true, this would suggest that doping of p(g3T2-T) and p(g4T2-T) is associated with charge formation first in ordered region. Meanwhile, the polymer with the different side chain substitution pattern, p(g2T2), does not show this sort of charging of ordered
regions because it lacks such heterogeneity. While highly speculative, this picture would be consistent with the electrochemical properties and the unstructured absorption spectrum of p(g2T2), which is indicative of disordered and uncoupled chromophore segments.

Figure 4.2.6 – Potential-dependent absorption spectra of A) p(g2T2-2), B) p(g3T2-T), C) p(g4T2-T), D) p(g6T2-T), and E) p(g2T2) films cast on ITO/glass in 0.1 M NaCl/H2O. Dash lines represents as-cast film. Spectra are recorded every 100 mV, following the color gradient. The figure has been adapted with permission from the literature\textsuperscript{368} and modified. © 2020 American Chemical Society.
The overall absorption intensity of the polaronic band is structure-dependent, as well. The polaronic bands of p(g4T2-T) have lower relative intensity than those of polymers p(g3T2-T) and p(g2T2). Presently, there are no known relationships governing such differences in polaron intensity (i.e. polaron concentration and oscillator strength) in electrochemically doped CPs.

Upon further oxidation to +0.8 V, all polymers exhibit minimal absorption in the visible range (Figure 4.2.6). This indicates that all materials, despite their different C* values and side chain structures, can be virtually completely p-doped within the electrochemical window of water. At these high potentials, there is minimal absorbance of the π-π* transition (~550-650 nm), indicating that little neutral chromophore remains in the film. As mentioned before, the cyclic voltammograms of polymers p(g3T2-T) and p(g4T2-T) show significant capacitive charging characteristics beyond +0.3 V. For these materials, spectral changes continue within the broad capacitive window of the CV (Figure 4.2.2A), suggesting that at least a portion of current passed in this range is faradaic in origin.

Similarly, the energy and absorption intensity of the bipolaronic states (>1400 nm) vary among the polymers. Theoretical and experimental work has suggested that the positioning, shape, and oscillator strength of the these charge carrier bands (both chemically induced and photo-induced) can be related to a host of interrelated factors, such as to the extent and nature of two-dimensional carrier delocalization, polymer crystallinity and molecular weight, and the distance between the counter-ion and the charge carrier.\textsuperscript{395–400} In the present study, the process underlying these spectral differences are not entirely clear. Because no techniques were used to probe these charged states any further, no comments can be made regarding the origin of these differences. At the very least, these
data show that the nature of the charge carrier and its coupling to the polymer lattice seem to depend on the factors dictated by the length of the EG side chain.

Following spectroelectrochemical studies, a negative potential (-1.0 V) was applied to re-reduce the films to their neutral states. All polymers did not fully recover the same \( \pi-\pi^* \) absorption intensity after re-reduction (~600 nm), as shown by the red traces in Figure 4.2.6A-D. For polymers (pg3T2-T) and (g4T2-T), the intensity of the “recovered” neutral absorption after the spectroelectrochemistry was sometimes enhanced and sometimes diminished relative to the original neutral absorption intensity. For these polymers, the reduction in \( \pi-\pi^* \) absorption intensity is not accompanied by any residual polaron absorption, which excludes the possibility of trapped charges in the film. These changes in the neutral absorption intensity could be due to: (i) a change in oscillator strength of the \( \pi-\pi^* \) transition, which is typically arises from changes in chain conformation, or (ii) degradation of the polymer, or (iii) uncontrolled variations in electrolyte oxygen content or pH, which may in turn result in (i) or (ii).

For polymers p(g6T2-T), the reduced absorption intensity of the neutral polymer was consistent and explicable. As previously described, the p-doped form of p(g6T2-T) dispersed in the aqueous electrolyte, so the poor recovery of the \( \pi-\pi^* \) absorption intensity likely due to additional lost polymer diffusing away in the electrolyte. For polymer p(g2T2-T), the inability to fully recover the \( \pi-\pi^* \) absorption at -1.0 V intensity is also accompanied by additional trapped charges, as evidenced by the contaminant increase in the residual absorption of trapped polarons in the NIR.
While some conclusions can be drawn from the absorption spectra of the glycol-functionalized PTs, there remain many unaddressed features and trends that could potentially inform a more comprehensive understanding of the material properties. Without a deeper investigation into these newly synthesized polymers, one cannot draw strong or quantitative conclusions from the absorption spectra. Relating these optical signatures (especially those of the electrochemically induced charged states) to polymer structure and conformation remains a worthwhile endeavor for a future study.

4.2.4 Thin Film Microstructure

A more complete picture of the interrelated factors governing the properties of these materials can be obtained by X-ray scattering techniques, which shed light on the long-range ordering of the films in the solid state. It is important to note that the design rules for OECT active materials are still rather ambiguous. In the field, there are reports of high-performing amorphous OECT materials\textsuperscript{227} as well as examples demonstrating how disordered microstructures can promote electrolyte uptake, doping efficiency, and ultimate transport.\textsuperscript{370,401} Meanwhile, there are also reports showcasing how enhanced crystallinity and order in the active material can improve OECT performance.\textsuperscript{223,402,403} It is likely that these relationships are not directly causal. Instead, the design of high-performing OECT materials probably depends on the interplay of: (i) the length scale of said order, (ii) the energetic favorability specific polymer-ion interaction, which may outweigh the barrier to ion transport typically imposed by a particular microstructure, and (iii) the coupling of ionic and electronic charges in the bulk of the film. Given this ambiguity, evaluating the microstructure of the polymers studied here was still deemed a worthwhile effort.
Grazing-incidence wide angle x-ray scattering (GIWAXS) was performed to evaluate the microstructure of the films, revealing noticeable differences in the long-range order depending on the length and substitution pattern of the EG-based side chains. All samples were blade coated as described in CHAPTER 3.5, except p(g2T2-T), which was spray-cast from a warm solution due to poor solubility. Representative two-dimensional scattering patterns are shown in Supporting Figure 4.4.4 through Supporting Figure 4.4.8. Intensities are normalized to film thickness for all polymers except for p(g6T2-T), which was too soft for thickness determination by profilometry. Sine-corrected line cuts were used to identify scattering peaks, which are tabulated for each polymer in Supporting Table 4.4.1 through Supporting Table 4.4.5. As described previously in CHAPTER 2.5.1, interpretations of GIWAXS patterns can be very ambiguous, especially for new materials like the EG-functionalized PTs studied in this work. Accordingly, interpretation of GIWAXS data, including lattice assignment, is based on reports in the literature for similar PTs and therefore is rather speculative. Further studies are required to conclusively assign and interpret the scattering features.

The scattering pattern of p(g2T2-2) (Supporting Figure 4.4.4), which has the lowest side chain density, is comprised of four strong isotropic scattering signals with no preferred orientation. In the line cut, an additional weak scattering peak is observed at high q (~1.8 Å\(^{-1}\)). The four isotropic scattering features are relatively narrow compared to what is typically observed for CP films, representing some periodicity with a relatively large coherence length and little dispersion. These uniform scattering arcs are highly unusual for CPs, as they more closely resemble the Debye-Scherrer rings observed in the diffraction patterns of randomly oriented, polycrystalline, “powder-like” materials. Because this
polymer was so insoluble, it was spray-cast from a hot chloroform/chlorobenzene solution. The isotropic and relatively sharp GIWAXS pattern may suggest that the material perhaps was not fully dissolved upon casting, but instead was spray-cast as a dispersion of aggregates. As mentioned above, there is a single weak peak at $q = 1.81$ Å. While we cannot definitively assign this feature without further in-depth analysis, this feature is tentatively assigned as scattering from π stacking ($d_{(020)} = 3.6$ Å). This is a speculative assignment based on similarity of the peak shape and position to the established π-stacking reflections observed in P3HT ($d_{(020)} \approx$ c. 3.8 Å).\textsuperscript{196,311,312,404,405} Given the unusual scattering pattern and processing conditions associated with p(g2T2-T), no further conclusions will be drawn regarding its microstructure.

When evaluating the scattering patterns of the remaining polymer films, Supporting Figure 4.4.5 through Supporting Figure 4.4.8), we note that all GIWAXS patterns show a broad, isotropic scattering “halo” at $q = 1.4–1.6$ Å$^{-1}$ (d ≈ 4 Å). It is important to emphasize that this smeared scattering arc does not correspond to π-π stacking. In fact, many things can scatter at this q value (as described in CHAPTER 2.5.1). When studying thin films of PTs, this halo is commonly attributed to side chain disorder.\textsuperscript{311} Evidence of π-π stacking and other lattice parameters typically are either superimposed on this halo or fall at slightly higher q.

As can be seen in the scattering patterns, the overall scattering intensities of polymers p(g3T2-T) and p(g4T2-T) are the highest, suggesting that these films are composed of the greatest fraction of material with long-range order (Supporting Figure 4.4.5 and Supporting Figure 4.4.6). These polymers show very intense scattering in the $q_z$ direction, corresponding to what is speculatively assigned as face-on π-π stacking (indexed
and lamellar ordering (indexed (100)) (Supporting Table 4.4.2 and Supporting Table 4.4.3). Interestingly, the intense face-on (020) scattering in the out-of-plane direction is not complemented by a strong lamellar spacing in the in-plane direction, as would be suspected in a polythiophene crystallite with three-dimensional order (see unit cell in Figure 2.5.1B). This suggests that two unique populations diffracting species may exist in the film and/or that periodicity dominates in only one dimension.

In addition to the out-of-plane (020) scattering, polymer p(g3T2-T) also displayed an in-plane (020) scattering peak, therefore indicating that p(g3T2-T) assumes a mixed face on/edge on orientation, while p(g4T2-T) solely adopts a face on-orientation. These findings are consistent with literature demonstrating that polymers with higher solubilities in the processing solvent prefer to orient in a face-on rather than edge-on textures, all else being similar.\textsuperscript{406,407}

Assuming the hypothesized assignments above are correct, p(g3T2-T) and p(g4T2-T) show strong $\pi-\pi$ stacking distances of 3.5 and 3.6 Å, respectively (Table 4.2.4). While this is a bit smaller than the $\pi-\pi$ stacking distance observed for P3HT, it is similar to the $\pi-\pi$ stacking distances observed for thin films of PBTTT.\textsuperscript{408} These peaks are also sharp, representing a high coherence length (full Scherrer analysis could not be performed due to convolution from other scattering signals). In fact, for p(g4T2-T), a higher-order scattering peak corresponding to twice the speculated $\pi-\pi$ stacking distance ($d_{(010)} = 7.1$) was observed in the $q_x$ direction. It is rather interesting that the polymer with longer side chains actually shows enhanced $\pi$ stacking; this could potentially be due to the g4 side chains somehow inducing a chain conformation that is favorable for ordering. Alternatively, these longer side chains may slow the precipitation of the polymer from solution by enhancing
solubility, thereby allowing more time for intermolecular arrangement. While the UV-Vis and GIWAXS trends cannot be rigorously related, as the two measurements probe different length scales of order, it is interesting to note that the relatively weaker π stacking in \( p(\text{g3T2-T}) \) is associated with the blue-shifted broadening of the UV-Vis absorption spectrum for this polymer (Figure 4.2.5), which at least paints a consistent picture.

Increasing the side chain length from three ethylene oxide units in \( p(\text{g3T2-T}) \) to four ethylene oxide units \( p(\text{g4T2-T}) \) is an associated with an expected increase in lamellar spacing by about 10 Å (Table 4.2.4). This is consistent with the addition of three atoms per side chain (six atoms per lamellae). Polymers \( p(\text{g3T2-T}) \) and \( p(\text{g4T2-T}) \) also show second-order lamellar scattering peaks (200) in the out-of-plane direction, which was indicative of regular ordering of side chains within the lamellae.

**Table 4.2.4 –** Orientational texture and speculated lattice parameters corresponding to the π-π stacking distance (\( d_{020} \)) and lamellar spacing (\( d_{100} \)) for films of EG-functionalized polythiophenes. Spacing was extracted from out-of-plane (\( q_z \)) GIWAXS scattering, unless otherwise noted.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Texture</th>
<th>( d_{020} ) (Å)</th>
<th>( d_{100} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p(\text{g3T2-T}) )</td>
<td>Mixed</td>
<td>3.6</td>
<td>16.5(^a)</td>
</tr>
<tr>
<td>( p(\text{g4T2-T}) )</td>
<td>Face-On</td>
<td>3.5(^a)</td>
<td>27.3(^a)</td>
</tr>
<tr>
<td>( p(\text{g6T2-T}) )</td>
<td>Edge-On</td>
<td>3.7(^b)</td>
<td>24.2(^a)</td>
</tr>
<tr>
<td>( p(\text{g2T2}) )</td>
<td>Mixed</td>
<td>3.6(^b)</td>
<td>15.3(^{a,b})</td>
</tr>
</tbody>
</table>

\(^a\) Shows higher-order reflections.
\(^b\) Extracted from scattering in \( q_{xy} \) plane.

Note: All values represent average distances calculated from two separate films, cast and measured separately. Std. err. < 0.1 Å.
Further increasing the side chain length by two additional ethylene oxide units in p(g6T2-T) has substantial microstructural consequences. First, virtually all π stacking of the PT backbone is suppressed (Supporting Figure 4.4.7). There is only a faint in-plane peak at q = 1.71 Å\(^{-1}\) that could be hypothesized arises from weak π scattering, with d\(_{(020)}\) = 3.7 Å (Supporting Table 4.4.4 and Table 4.2.4). Despite the side chains in p(g6T2-T) being approximately six atoms longer than p(g4T2-T), the (100) lamellar reflection actually shifts to higher q (Supporting Table 4.4.4). This corresponds to a decrease in lamellar spacing from ~27 Å in p(g4T2-T) to ~24 Å in p(g6T2-T), even though the side chains in p(g6T2-T) are longer. This result could arise from two scenarios: (i) The long EG-based side chains in p(g6T2-T) interdigitate, or (ii) the side chain tile angle has changed. Both (i) and (ii) would result in a reduction of d\(_{(100)}\). Without further analysis, we cannot exclude either option. However, based on the observation that rather strong second- and third-order lamellar reflections are observed in p(g6T2-T) (Supporting Table 4.4.4), indicating regular ordering within the side chains, we hypothesize that the reduction in d\(_{(100)}\) is primarily the result of side chain interdigitation. Such interdigitation may be induced by dipolar interactions originating from the C-O bonds in the side chain.

In sum, the optimal intermediate side chain lengths in p(g3T2-T) and p(g4T2-T) are ideal for promoting processability while also allowing for long-range ordering of the π-conjugated active material in the solid state. Meanwhile, in p(g6T2-T), the side chains are so long that that the microstructure of the film is determined by side chain interactions within the lamellae, rather than being driven π-stacking.

In addition to the side chain length, the side chain substitution pattern also greatly influences the microstructure of these materials. Polymer p(g2T2), which has a side chain
on every thiophene rings, shows markedly less order than the analogues with side chains on only 2/3 of the thiophene rings. This is evidenced by its low thickness-normalized scattering intensity (Supporting Figure 4.4.7) compared to p(g3T2-T) and p(g4T2-T). The GIWAXS scattering pattern of p(g2T2) also exhibits a relatively isotropic scattering profile. Any scattering that could potentially be attributed to π stacking ($q = 1.72 \, \text{Å}^{-1}$, Supporting Table 4.4.5) was only barely detectable.

There are numerous studies documenting the effects of side chain structure and length on the microstructure of conjugated polymer films. Among these, some studies have hypothesized that the addition of longer or interacting side chains to the conjugated backbone can distort the planarity of the polymer chain and obstruct the intermolecular ordering of the backbone. By comparing p(g2T2) and p(g3T2-T), we also find evidence showcasing the importance of the side chain substitution pattern. Even when the side chains are lengthened (as in p(g3T2-T)), or when the overall side chain density is higher (as in p(g4T2-T)), superior ordering can be attained by simply changing the distribution of the side chain density on the backbone. Specifically, localizing the side chain functionality on fewer aromatic units induces greater solid-state order when compared to a system with side chains evenly distributed across the backbone.

However, these trends only hold true within a finite range of side chain lengths. For polymer p(g6T2-T), which has a seemingly favorable substitution pattern but extremely long side chains, the side chain interactions appear to be so dominant that they seem to dictate film solidification and reduce π stacking of the backbone. This observation is similar to a very comprehensive study by Carpenter et al., in which optical, thermal, and
X-ray techniques were used to investigate the trade-off between side chain and backbone ordering in a donor-acceptor CP.\textsuperscript{410}

As explained previously, the GIWAXS characteristics cannot be rigorously related to results from the electrochemical and optical studies. As a diffraction technique, GIWAXS relies on appreciable coherent periodicity and therefore is sensitive to longer-range order. Meanwhile, electrochemical and optical characteristics (e.g. $E_{\text{ox}}$, $E_{\text{opt}}$) are sensitive to molecular-level characteristics, such as planarization and/or cofacial stacking of chromophore segments. That being said, the differences in the EG-functionalized PTs studied in this chapter support a self-consistent trend. We observe that the unsubstituted “spacer” thiophene in the p(gxT2-T) series promotes longer-range ordering in the solid state (especially by enhancing $\pi-\pi$ stacking) compared to the polymer with every thiophene functionalized with a side chain. This improved microstructure may facilitate inter-chain interactions that lower the ionization potential and assists in charge carrier formation. Because doping is associated with enhanced order in the $(0k0)$ direction,\textsuperscript{196,320,411} polymers with greater coherence in this direction may undergo electrochemical doping more easily, as there is less of an energetic barrier associated with geometric reorganization.

We also observe that differences in short-range order are supported by the UV-Vis. Such differences in intermolecular order could explain the unexpected similarities in the $E_{\text{ox}}$ for p(g3T2-T) and p(g2T2), despite differences in their expected electron richness.

In the case of these EG-functionalized PTs, we observe that enhanced solid-state ordering (as in the case of p(g3T2-T) and p(g4T2-T)) appears to be associated with greater redox capacitance and stability. It has been experimentally shown that crystalline regions
in polythiophenes have a lower $E_{\text{ox}}$ than amorphous domains$^{255,257}$ (all else being equal), which is consistent with fundamental expectation that more ordered materials have longer “effective conjugation lengths” through enhanced inter- and intra-molecular interactions. Here, we show that the polymers capable of adopting more ordered conformations with tighter $\pi$ stacks appear to also exhibit a higher charge storage capacity. This manifests in both the volume- and mass- normalized capacitance, suggesting an intrinsic enhancement of charge stabilization and doping density. A similar relationship has been observed for redox-active PANI nanofibers, where highly anisotropic structures showed greater capacitance.$^{412}$ This result is especially interesting considering the origin of the “capacitive plateau” in conjugated polymers. Evidently, the intermolecular ordering play a role in determining not only the steady-state capacitance by EIS but also the shape of the CV $i-V$ characteristics. It is possible that the ability to delocalize charges in two dimensions allows for additional unique oxidation steps, as charges are formed along and between chains. This would contribute to the presence of multiple “overlapping” redox processes, as has been discussed in previous literature.$^{58,256}$

From this work, we observe that enhanced intermolecular ordering (both short- and long-range) can be achieved simply by redistributing the side chain density along the backbone. We speculate that the unsubstituted “spacer” thiophene plays a unique role in enhancing intermolecular interactions, which are critical for the formation and stabilization of charges in two dimensions. We emphasize that these are proposed explanations, and that further studies would be required to systematically study these effects $\textit{in situ}$ upon electrochemical doping.
The GIWAXS results also support (albeit do not prove) the previous hypothesis regarding the origin of the stability differences between (pg3T2-T) and p(g2T2). The greater ordering in p(g3T2-T) relative to p(g2T2) may exclude excess electrolyte and potential nucleophiles from entering the film and reacting with the π system. Alternatively, the ordering could contribute to enhanced stabilization of charge carriers, thus making side reactions and degradation less favorable. Further work would be required to prove these hypotheses unambiguously.

An important limitation of the GIWAXS results reported in this chapter is that data was collected on pristine dry films, which may not represent the microstructure of the film after doping/de-doping in an electrolyte. It is expected that the GIWAXS patterns and scattering intensities would change in response to ions/solvent intercalation into the polymer and any geometric reorganization induced by charge carrier generation. Nonetheless, these GIWAXS results provide a starting point for broadly comparing the effect of side chain length on the solid-state ordering of the materials.

4.3 Conclusions

4.3.1 Summary of Findings

Replacing the alkyl side chains on conventional semiconducting polymers with ethylene glycol (EG)-based chains is a successful strategy for the molecular design of conjugated polymers for bioelectronic devices, including organic electrochemical transistors (OECTs). Such polymers demonstrate the capability to conduct both ionic and electronic charges and may offer superior performance compared to the most commonly
used active material, PEDOT:PSS. Many research efforts have been dedicated to optimizing OECT performance through the modification of the CP backbone (e.g. using backbones comprised of thiophene, thienothiophene, benzenedithiophene, dioxythiophene, pyrrole, and donor-acceptor repeat units), as discussed earlier in CHAPTER 1.3.2.3. However, variation of the EG chain length and substitution pattern onto the backbone has not been systematically investigated to an appreciable degree.

In this work, we report and investigate a series of so-called “glycolated” polythiophenes (PTs) with pendant EG-based side chains spanning two to six ethylene oxide (EO) repeat units. This series allows us to study the effect of side chain length on the electrochemical, optical, and microstructural properties of polythiophene-based OECT active materials. A careful balance in the EG side chain length must be achieved during the design of EG-functionalized conjugated polymers for OECTs. This work focuses on understanding polymer functionality specifically when electrochemically doping in an aqueous NaCl electrolyte, as these conditions represent a relevant environment for biological sensing with OECTs.

As determined by cyclic voltammetry, EIS, and spectroelectrochemistry performed in an aqueous electrolyte, each of the polymers can be oxidized (p-doped) and reduced (de-doped). However, significant variations in the redox properties of the materials were noted. We observed that there is an optimal intermediate glycol side chain length for promoting processability, redox activity, and stability. Polymer p(g2T2-T), which has the lowest side chain density and shortest side chain length, suffers from remarkably poor solubility and inadequate redox activity in aqueous media. Meanwhile, the long side chains in p(g6T2-T) result in dispersion and instability in the aqueous electrolyte, demonstrating that over
relatively small changes in side chain length, there is a “sweet spot” where polarity and stability mutually maximized. Moreover, interactions between these long side chains dictate the formation of extensive lamellar structures while suppressing long-range ordering of the π system.

Polymers with intermediate side chain lengths—(p(g3T2-T) and p(g4T2-T)—are sufficiently polar for aqueous redox activity in water without dispersing or delaminating in the electrolyte. In particular, the triethylene glycol-functionalized polymer, p(g3T2-T), passes the highest amount of charge and exhibits the greatest peak C* of all polymers tested (~210 F cm\(^{-3}\)). Shortening and lengthening the side chain beyond this optimal size proved detrimental, suggesting that a careful balance in the EG length must be achieved during the design of CPs to maximize their charging capabilities for OECTs. Curiously, this polymer p(g3T2-T) was among the first EG-based PTs to be used in OECTs,\(^{203}\) and here we show that this material also happens to have the optimal side chain length when it is systematically compared against other analogues.

In addition to exploring the effect of side chain length, this work also establishes the critical role that the side chain substitution pattern can have on ultimate material properties. Functionalization of every thiophene ring with side chains (as in p(g2T2)) yields a material with lower capacitance when compared to p(g3T2-T), which has only 2/3 of the thiophene rings substituted, despite these two materials having similar electroactive masses. Even for p(g4T2-T), which has a considerably lower relative electroactive mass than p(g2T2) (37% vs. 50%, respectively), the side chain substitution pattern in p(g4T2-T) yields a significantly enhanced C*. Clearly, the incorporation of the minimally substituted
thiophene “spacer” into the backbone of these materials is critical for enhancing electrochemical stability and capacitance, even when side chains are lengthened.

We further relate these differences in redox properties to the UV-Vis absorption spectra of the polymers. Polymers containing these “spacer” units show red-shifted absorption spectra with enhanced vibronic structure, suggesting that this substitution pattern enhances the molecular ordering in the solid state. GIWAXS results shows that these differences in ordering persist over longer scales, as well, with p(g4T2-T) and p(g3T2-T) showing more pronounced texture and greater π spacing compared to p(g2T2). An important limitation of these measurements lies in the fact that the GIWAXS was performed on pristine, as-cast films, not films that are electrochemically biased in the aqueous media. Therefore, even if the length scales probed by GIWAXS are relevant for OECT material design (which is presently unclear), the pristine film GIWAXS likely does not represent the microstructure of the film in an actual OECT device, where ions and solvent are expected to cause substantial disruption.

From these results, we hypothesize that the enhanced redox properties of the p(gxT2-T) grafting pattern relative to the p(gxT2) pattern are associated with improved intermolecular ordering, which lowers E_{ox} and stabilizes charge carriers by virtue of enhanced aggregation. A similar strategy was recently reported by Li et al. to enhance the chemical doping in polythiophene copolymers. In this study, the incorporation of a thienothiophene spacer unit into the backbone along with longer pendant side chains was shown enhance doping efficiency and solid-state conductivity.
In sum, five EG-functionalized polythiophenes were developed for OECT applications. These materials characterized to investigate the influence of side chain length and substitution pattern on the final redox, optical, and microstructural properties of the material.

4.3.2 Relation to OECT Devices

While the results in this chapter chiefly relate to the fundamental material properties, some of PTs reported here were later incorporated into planar aqueous OECTs to evaluate the associated device performance. Only devices with the p(g_xT2-T) series were tested. These results, which were recently published,\textsuperscript{368} show that the device characteristics trend nicely with the C* trends identified in this chapter. Devices with p(g3T2-T) performed the best (highest normalized g_m), followed closely by p(g4T2-T). Devices fabricated with a p(g2T2-T) active layer were found to perform quite poorly, which is reflective of this material’s low C* identified here. Meanwhile, as expected, polymer p(g6T2-T) was not able to be integrated into any operational OECT, as it dispersed in the aqueous electrolyte.

Because the device characteristics of p(g2T2) were never evaluated, we cannot conclusively determine whether the structure-property relationships regarding side chain substitution pattern translate to meaningful differences in device performance. However, similar concept was recently tested by Moser et al., who used an analogous approach to study the role of side chain distribution on OECT performance. While there was no consistent trend observed across the family of four polymers reported in this study, the
authors did note that OECT performance and stability can be enhanced by changing the manner in which side chain density is grafted on the polymer backbone.\textsuperscript{416}

Finally, if the origin of the enhanced C* for p(g3T2-T) and p(g4T2-T) relative to p(g2T2) is in fact causally related to enhanced “order,” one would expect to observe similar enhancement in C* through the use of processing techniques that induce aggregation in the film. This concept was demonstrated by Savva et al., who studied the role of solvent quality on the properties and associated device performance of EG-functionalized n-type OECT active materials.\textsuperscript{402} The authors noted that increasing the amount of poor solvent in the casting solution resulted in films with higher C* and devices with enhanced $g_m$, up to a certain point. However, these authors did not study the gravimetric capacitance alongside C* to determine if the effect arose solely from density differences. Moreover, it is unclear how such processing-induced changes in film order can be maintained upon repeat doping/de-doping reactions. There remains much to be explored in this respect.
4.4 Supporting Figures

Supporting Figure 4.4.1 – DPV traces (solid lines) for drop-cast films of A) p(g2T2-T), B) p(g4T2-T), C) p(g2T2-T), D) p(g6T2-T), and E) p(g2T2) in degassed 0.1 M NaCl/H2O. The dashed lines show the approximated baseline and offset tangents. The two oxidation onsets, given as the intersection of these two fits, onsets are labeled. Panels A-D have been adapted with permission with permission from the literature. © 2020 American Chemical Society.
Supporting Figure 4.4.2 – A) Scan rate dependent CV data for drop-cast films of p(g6T2-T) in 0.1 M NaCl/H₂O. Each curve represents the tenth cycle out of ten scans performed at each scan rate. B) Normalized data from (A) for comparison.
Supporting Figure 4.4.3 – Charge retention for p(g3T2-T) films drop-cast on a glassy carbon button electrode and cycled repeatedly between -0.5 and +0.8 V vs. Ag/AgCl in degassed 0.1 M NaCl/H₂O under an inert argon blanket.
Supporting Figure 4.4.4 – A) Two-dimensional representative GIWAXS pattern for p(g2T2-T) spray-coated in Si. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale. B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing \((hkl)\) labeled.

Supporting Table 4.4.1 – Peaks identified from the representative GIWAXS pattern of p(g2T2-T) shown in Supporting Figure 4.4.4, along with corresponding \(d_{hkl}\) spacing and speculated assignment, if applicable.

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Supporting Figure 4.4.5 – A) Two-dimensional representative GIWAXS pattern for p(g3T2-T) blade-coated in Si. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale. B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled. This figure has been adapted with permission with permission from the literature.© 2020 American Chemical Society.

Supporting Table 4.4.2 – Peaks identified from the representative GIWAXS pattern of p(g3T2-T) shown in Supporting Figure 4.4.5, along with corresponding $d_{hkl}$ spacing and speculated assignment, if applicable. Amorphous halo at $q \approx 1.5$ Å$^{-1}$ is excluded.

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Supporting Figure 4.4.6 – A) Two-dimensional representative GIWAXS pattern for p(g4T2-T) blade-coated in Si. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale. B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled. This figure has been adapted with permission with permission from the literature. © 2020 American Chemical Society.

Supporting Table 4.4.3 – Peaks identified from the representative GIWAXS pattern of p(g4T2-T) shown in Supporting Figure 4.4.6, along with corresponding d_{hkl} spacing and speculated assignment, if applicable. Amorphous halo at q ≈ 1.4 Å^{-1} is excluded.

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Supporting Figure 4.4.7 – A) Two-dimensional representative GIWAXS pattern for p(g6T2-T) blade-coated in Si. Scattering intensities are represented linearly, following a purple-red color scale. B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled. This figure has been adapted with permission with permission from the literature.© 2020, American Chemical Society.

Supporting Table 4.4.4 – Peaks identified from the representative GIWAXS pattern of p(g6T2-T) shown in Supporting Figure 4.4.7, along with corresponding d_{hkl} spacing and speculated assignment, if applicable. Amorphous halo at q ≈ 1.5 Å⁻¹ is excluded.

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Supporting Figure 4.4.8 – A) Two-dimensional GIWAXS pattern for p(g2T2) blade-coated in Si. Scattering intensities are represented linearly, following a purple-red color scale. B) In- and out-of-plane linecuts of scattering data in panel A, with hypothesized lattice spacing (hkl) labeled.

Supporting Table 4.4.5 – Peaks identified from the representative GIWAXS pattern of p(g2T2) shown in Supporting Figure 4.4.8, along with corresponding d_{hkl} spacing and speculated assignment, if applicable. Amorphous halo at q \approx 1.6 Å⁻¹ is excluded.

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4.5 Additional Experimental Details

Aqueous cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a Reference 3000 Gamry potentiostat/galvanostat/ZRA controlled with Gamry Framework 6.5 software. For CV and PV, samples were prepared by dissolving and drop-casting identical masses of each polymer (16 μg) onto a polished glassy carbon button electrode (a = 0.07 cm$^2$). All polymers except for p(g2T2-T) were dissolved at a concentration of 4 mg mL$^{-1}$ and drop-cast in four 1-μL aliquots. The polymer p(g2T2-T) was dissolved in warm (50 °C) chlorobenzene at 2 mg mL$^{-1}$ and drop-cast in four 2-μL aliquots. All aqueous electrochemistry was performed in a 0.1 M solution of NaCl (biotechnology grade, Amresco) dissolved in ultrapure water (18.2 MΩ·cm) while under an argon blanket. Prior to electrochemical studies, the electrolyte was degassed with argon for ten minutes. For CV and DPV, a glassy carbon rod was used as the counter electrode, and an Ag/AgCl electrode (3 M NaCl/H$_2$O inner solution, BASi) was used as the reference. For both measurements, a three-electrode configuration involving a Princeton Applied Research 273A potentiostat/galvanostat was used.

For spectroelectrochemical measurements, all polymers were cast on ITO/glass substrates. Prior to coating, the substrates were cleaned by sonicating a solution of sodium dodecyl sulfate in DI water, followed by subsequent sonication in neat DI water, acetone, and isopropanol. Substrates were then dried under an argon stream and then cleaned for 10 minutes in a UV-O$_3$ chamber. Polymers p(g3T2-T), p(g4T2-T), and p(g6T2-T) were dissolved at 20 mg mL$^{-1}$ in room temperature chloroform and blade coated using a custom-built blade coater. The blade consisted of a clean and unmodified glass slide with a gap height of 150 μm and a blade speed of 4 mm s$^{-1}$. The substrate was heated to 30 °C during
coating. Due to solubility limitations, polymer p(g2T2-T) was spray-cast from a 0.5 mg mL⁻¹ solution in a solvent mixture of 1:1 chlorobenzene:chloroform heated to 50 °C. Spray casting was performed using an Iwata-Eclipse HP-BC airbrush with argon (40 psi) as the carrier gas.

Potential-dependent UV-vis-NIR absorption spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer in conjunction with a Princeton Applied Research 273A potentiostat/galvanostat with CorrWare software. The polymer-coated ITO electrodes were immersed in a quartz cuvette and incorporated into a three-electrode cell. The polymer-coated ITO was the working electrode, a platinum flag served as the counter electrode, and an Ag/AgCl (3 M NaCl/H2O inner solution, BASi) was used as the reference. The electrolyte was a 0.1 M NaCl solution in ultrapure water (18.2 MΩ·cm). As-cast spectra were recorded at open circuit conditions immediately upon immersing the film in the electrolyte without any external bias. Prior to spectroelectrochemical measurements, the polymers were subject to 10 cyclic voltammograms (-0.5 to +0.8 V at 50 mV s⁻¹) to electrochemically condition the film. Spectra were recorded under potentiostatic conditions in 100 mV increments. Before recording the spectra, the film was held at each respective potential for 10–30 seconds, until the current transient reached a steady state.

Electrochemical impedance spectroscopy (EIS) was performed as described in CHAPTER 2.3.4 on a Reference 3000 Gamry potentiostat/galvanostat/ZRA controlled with Gamry Framework 6.5 software. Rectangular films were cast onto clean ITO/glass electrodes in the same manner described for the spectroelectrochemical studies. The polymer-coated ITO electrode was used as the working electrode, while a large stainless-steel plate serving as the counter electrode and Ag/AgCl electrode (3 M NaCl/H2O inner
solution, BASi) was used as the reference. The cell was completed with a 0.1 M NaCl solution in ultrapure water, degassed with argon and kept under an argon blanket throughout the entirety of the EIS studies. The working and counter electrodes were positioned 1 cm apart, with the polymer-coated side of the ITO electrode directly facing the stainless-steel plate. The reference electrode was positioned between the two electrodes at a height such that the reference electrode was not obstructing ion flow between the working and counter. The electrodes were held in place throughout the duration of the study using a custom-built fixture.

Prior to performing EIS studies, the films were electrochemically conditioned via 10 cyclic voltammograms. A 5 mV AC bias was superimposed on a range of DC offsets, which set a particular doping level in the polymer film. Film were held at a given potential for 60 s before recording the EIS spectra to ensure steady-state behavior, starting with the film in its most reduced state and increasing incrementally to its most oxidized state. EIS was performed at low frequencies (10 Hz–0.1 Hz) to capture the capacitance associated with the faradaic doping/de-doping reaction. The experimental impedance spectra were fitted using the Zview software (Scribner Associates Inc., USA). The low-frequency portion of the impedance spectrum was fit with an R-CPE series circuit, and C was calculated as described in CHAPTER 2.3.4.

After EIS, the films were de-doped, rinsed with copious amounts of DI water, and dried. The film thickness was measured using a Bruker Dektak XT profilometer. The film length and width were calculated using calipers and used to calculate the overall volume of the dry film. The calculated capacitance, C, was normalized to film thickness, affording
the volumetric capacitance, $C^*$. Error bars represent the standard deviation of $C^*$ values calculated for 3+ unique films.

For grazing-incidence wide angle x-ray scattering (GIWAXS) measurements, films were cast on polished Si wafers under conditions identical to those used for preparing EIS and spectroelectrochemistry samples. GIWAXS was performed at the Stanford Synchrotron Radiation Lightsource (SLAC National Accelerator Laboratory) at beamline 11-3. A beam energy of 12.7 keV was employed and the incident angle of the measurement was approximately 0.13°. The sample distance was approximately 250 mm. Scattering patterns were calibrated using a standard sample of LaB$_6$. Data was processed and analyzed as described in CHAPTER 2.5.1.
CHAPTER 5. POLAR POLY(PRODOTS) AS ACTIVE MATERIALS FOR AQUEOUS OECTS: EFFECTS OF SIDE CHAIN LENGTH AND FUNCTIONALITY

This chapter includes content partially adapted from the following two previously published works:


This chapter also includes unpublished content adapted from a working manuscript that is currently in preparation, as tentatively referenced below:

5.1 Introduction

5.1.1 OECT Active Materials

As described previously, $\pi$ conjugated polymers capable of electrochemically interfacing with aqueous and biological electrolytes are highly desirable for use in bio-electronic devices. Among these emerging technologies, the organic electrochemical transistor (OECT) shows tremendous potential for interfacing with biological systems due to its ability to transduce cellular ion fluxes (e.g. protons, metal ions, and neurotransmitters) into exogeneous electrical signal with extremely high signal fidelity. For a more comprehensive overview of OECTs, their working mechanism, and utility in biological sensing applications, the reader is directed to CHAPTER 1.3.2 and the references therein.

As the potential of OECTs in biological systems becomes increasingly apparent, there has been considerable effort devoted towards developing new aqueous-compatible, redox-active conjugated polymers that can interface with aqueous electrolyte. The development of these materials is also fundamentally important for developing a complete description of the electrochemical doping processes underlying OECT operation. There remains much to be learned regarding how polymer structure, macromolecular ordering, and specific polymer-ion interactions impact the so-called “mixed transport” of ionic and electronic charges in these redox-active systems.

In the pursuit of channel materials for p-type OECTs, the field has generally begun to move away from PEDOT:PSS for reasons explained earlier in this thesis (see CHAPTERS 1.3.2.3 and 4.1.2). Within the past decade, a number of p-type, aqueous-compatible CPs have been developed and targeted for OECT applications. These materials...
typically consist of a conjugated polymer backbone with highly polar (e.g. ethylene glycol-based) side chains. Based on certain metrics (e.g. C*), some of these materials have been reported to out-perform PEDOT:PSS. In addition, these alternative materials allow for more versatile synthetic modifications to the polymer backbone and side chains, which enables the development of comprehensive structure-property relationships.

For p-type and ambipolar devices, many OECTs active materials incorporate comonomers that are thought to induce ordering of the π-conjugated backbone for enhanced charge carrier mobility (e.g. thienothiophene, benzodithiophene (BDT), etc.) (see Figure 1.3.4A-D). However, this approach is not necessarily always desirable for designing polymers for electrochemical applications, seeing as these units may also result in poor solubility, high oxidation potentials, and irreversible degradation in water. For a BDT-based polymer (Figure 1.3.4B), the degradation mechanism is suggested to involve nucleophilic attack by water at radical cation sites, followed by the cleavage of polar chains and the formation of ketones adjacent to the backbone. This demonstrates that positioning the polar side chains directly onto an electron-poor repeat unit may render the polymer susceptible to irreversible degradation.

Additionally, while solid-state ordering induced by planar heterocycles may be beneficial for charge carrier mobility, generally speaking, polymer crystallinity generally speaking has been shown to obstruct ion transport. Therefore, such ordering may not be advantageous for promoting ion uptake required for electrochemical doping of CPs. For poly(3-hexylthiophene) (P3HT) and similar polythiophenes, it was shown that ions irreversibly disrupt crystalline film domains, which potentially could compromise the mobility and carrier transport. Related work on polar PTs found that increased crystallinity
and/or “ordering” is not unequivocally considered advantageous for transport in electrochemically doped systems. While CHAPTER 4 and other studies established that some level of ordering is associated with enhanced redox properties, this trend does not hold up in extreme cases. In sum, the importance of ordering across different length scales (molecular, mesoscale, and microscale) and the interplay of ordering and with mixed transport is not understood, as previously alluded to (see CHAPTER 4.2.4, pp. 185).

The solubility and processability of the polymer are also important when considering developing inexpensive or even printed OECT devices. From a processing standpoint, some of the ethylene glycol (EG)-functionalized polymers used in OECTs suffer from poor solubility, even in halogenated aromatic solvents such as chlorobenzene. This poor solubility also encumbers the synthesis, purification, and isolation of high molecular weight and low dispersity polymers. Moreover, many of these OECT materials (such as those reported in CHAPTER 4) are prepared via Stille cross-coupling polymerization involving organotin reagents and byproducts. Such organotin compounds are difficult to remove from the polymer completely, even after extensive purification. Organotin compounds are widely known to have negative health effects, thus precluding the ultimate use of these materials in biological systems.

5.1.2 PXDOTs for OECTs

For electrochemical applications, like OECTs, poly(3,4-alkylenedioxythiophene) (PXDOT) derivatives have several distinct advantages over commonly used PT analogues. Namely, they are typically much easier to oxidize owing to the disubstitution of π-donating oxygen atoms and exhibit high redox stability. Early studies on polyheterocycles, such as
PXDOTs, have hypothesized that the dissubstitution at the β positions of the backbone thiophenes affords steric protection against nucleophilic attack onto the π system. Consequently PXDOTs are considered much more stable than many simple PTs that lack this protective functionalization. Stability of these materials in aqueous and/or biological electrolytes, which are often rich with potential nucleophiles, is of fundamental application-level importance. Interestingly, the electrochemical cycling stability of OECT active materials has only recently become a subject of study.

Several PXDOT-based polyelectrolytes (e.g. PEDOT-S, Figure 1.3.4J) and polyelectrolyte complexes have been used as active materials in OECTs and showed exceptional redox stability. In addition, biEDOT-based copolymers with hybrid alkyl/ethylene glycol-based side chains were recently developed and showed enhanced substrate adhesion and robustness upon repeated cycling in OECTs.

In addition to these EDOT-based polymers, poly(3,4-propylenedioxythiophenes) (PProDOTs) constitute a class of PXDOTs that also show enhanced electron richness and redox stability. In particular, PProDOTs have been widely studied as soluble active materials for electrochemical supercapacitors and electrochromic devices. When compared to EDOT, the ProDOT repeat unit is protected by a 3,4-propylenedioxy bridge, as opposed to a 3,4-ethylenedioxy bridge in EDOT. Thus, ProDOT repeat units can be tetrahedrally and symmetrically substituted with side chains at the 2 position of the bridge, yielding highly soluble and macromolecules without tacticity upon polymerization. The propyl ring appended to the thiophene unit in ProDOT is also associated with less resonance stabilization from the adjacent oxygen atoms when compared to EDOT. Due to this difference, many PProDOTs have higher IEs when compared to PEDOT derivatives and
therefore are typically not fully doped in ambient conditions. Consequently, PPProDOTs may be attractive active materials for stable, accumulation-mode OECTs.

5.1.3 Objectives

Considering these advantages, herein we report a series of soluble ProDOT-based copolymers with polar functional groups as alternative active materials for aqueous-based OECTs. By evaluating the electrochemical properties of these materials in aqueous and physiologically relevant electrolytes, we aim to accomplish the three tasks described below.

The first goal of this work is to understand how side chain polarity and length influences the properties of a new family of polar ProDOT-based copolymers. These materials, which were designed for OECT applications, show redox activity in aqueous media. Polymers with various side chain lengths, ranging from two to four ethylene oxide units will be evaluated to establish how side chain structure impacts the electrochemical properties of the resulting polymers. This comparison will not only shed light on structure-property relationships in EG-functionalized PProDOTs, but it also will allow for these trends to be compared to those established for the PTs in CHAPTER 4.

Moreover, this work will also leverage a side chain de-functionalization process to access a high capacitance, aqueous-compatible polymer with alcohol-terminated side chains. This approach, which has previously been adopted for application in polymer-based electrochromics$^{130,131,224,436}$ and electrochemical supercapacitors$^{225,226}$ represents a potential avenue for targeting unique solution-processed and aqueous-compatible materials that are inaccessible by other means.
The last goal of this effort is to introduce polar PProDOTs as new channel materials for aqueous OECTs. Importantly, this work demonstrates the first instance of an OECT active material that is both (i) derived from the ProDOT repeat unit, and (ii) prepared by direct(hetero)arylation polymerization.

In sum, this work seeks to show that PProDOTs are robust, aqueous-compatible, and versatile active materials for OECTs. Through these efforts, we aim to contribute to the growing body of knowledge pertaining to the design of aqueous-compatible and redox-active CPs. The presentation of new polymers in this chapter will also expand the library of OECT active materials, which may be subsequently be used in growing field of organic bioelectronics.

5.2 Results and Discussion

5.2.1 Polymer Design and Preparation

5.2.1.1 Structural Design of Polar PProDOTs

Our material design strategy involves the development of several ProDOT-based alternating copolymers. Each polymer is comprised of two unique ProDOT comonomers. For all materials in the family, one of the ProDOT comonomers (referred to as 2,2-dimethylProDOT, or DMP) is symmetrically disubstituted at the 2 position with small methyl groups. The other comonomer used to synthesize the materials consists of a second ProDOT unit that is difunctionalized with different solubilizing side chains. These groups vary in length, functionality, and polarity. Polymers G2-DMP, G3-DMP, and G4-DMP include comonomers functionalized with highly polar EG-based side chains (Figure 5.2.1).
The side chains differ in their length and are composed of two, three, and four ethylene oxide units, respectively. For these EG-functionalized polymers, the polar side chain not only imparts solubility, but it also increases the hydrophilicity of the polymer, which facilitates uptake of aqueous electrolyte.

In these materials, the minimally substituted DMP unit is thought to both promote interchain interactions and potentially also reduce steric hinderance associated with planarization of the π-conjugated backbone, thus increasing charge storage capacity, lowering its oxidation onset (E_{ox}), and potentially improving carrier transport. As reported in CHAPTER 4, the incorporation of such minimally substituted “spacer” units, like DMP, is beneficial for designing OECT active materials.

Because the homopolymers of these EG-functionalized ProDOT units were found to be soluble in water upon electrochemical p-doping, the incorporation of the DMP unit also lowers the solubility of the final material. This allows for an optimal hydrophilic-hydrophobic balance to be achieved: the EG-functionalized unit confers sufficient polarity for hydration and aqueous electrolyte uptake, while the DMP unit prevents dissolution in the aqueous electrolyte by virtue of its short and non-polar side chains.

In addition to these EG-functionalized polymers, this work also includes an analogous ProDOT-based DMP copolymer functionalized with 2-butyloctylester side chains (BOE-DMP in Figure 5.2.1). While this material is not expected to exhibit high redox capacitance in saline due to the long aliphatic groups appended to backbone, the ester functionality in the side chain provides a synthetic handle for downstream modification.
These functional groups can be cleaved under acidic or basic conditions, yielding a polymer with increased polarity and aqueous redox activity.

Figure 5.2.1 – Repeat unit structures of polar ProDOT copolymers, showing A) 2,2-dimethyl-ProDOT (DMP) based backbone, and B) various polar side chains with corresponding polymer names.

Such side chain de-functionalization strategies have been leveraged to accesses aqueous-soluble and/or aqueous electrolyte-compatible PProDOTs. Typically, these approaches are applied to ester functionalities oriented to yield the corresponding poly(carboxylic acid) or poly(carboxylate), which may be processed from
water and treated with base, thereby rendering the film “solvent resistant.”\textsuperscript{224–226,234,436,438,439} However, given that the PProDOTs studied here are targeted for biological settings, which are typically buffered around pH = 7.4, such poly(carboxylic acid) derivatives are unsuitable. These conditions may cause significant deprotonation of pendant carboxylic acid groups (pKₐ ≈ 5 in H₂O), resulting in a water-soluble poly(carboxylate) that will likely dissolve in most biological media.

Therefore, in this study we will use the polymer BOE-DMP whose pendant ester functionalities are oriented to afford a polymer with alcohol functionalities (pKₐ ≈ 15 in H₂O) upon hydrolysis with base. The resulting material, herein referred to as polymer OH-DMP, is shown in Figure 5.2.1. We hypothesize that removal of the aliphatic ester groups will increase the overall hydrophilicity of the material and therefore promote aqueous redox activity in the product OH-DMP, as has been shown for similar systems.\textsuperscript{224,225}

When compared to purely aliphatic side chains, hydroxyl-terminated side chains have been shown to improve the transport of hydrated ions and promote electrochemical doping of polythiophenes in aqueous media.\textsuperscript{232} However, the aqueous redox activity of these hydroxyl-functionalized PTs is demonstrably lower than some of the corresponding EG-functionalized PTs. In the literature, it is commonly asserted that these long, polar glycol-based side chains are required for enhanced aqueous ion transport and redox activity.\textsuperscript{373} Comparison of OH-DMP against the Gₓ-DMP series will allow us to test this claim and establish how alcohol- and glycol-functionalized polymers compare in terms of their aqueous redox properties.
In the polymer OH-DMP, the hydroxyl groups are connected to the ProDOT repeat unit through a small methylene linkage. Thus, the conjugated backbone has a lower side chain density relative to G2-DMP, G3-DMP, and G3-DMP, which may enhance interchain interactions that are important for efficient charge storage and transport. We also hypothesize that removal of side chain density may also yield a material with $C^*$ exceeding that of the EG-functionalized polymers (Gx-DMP), as it will enhance the relative electroactive fraction of the film. Hydroxyl groups are also capable of hydrogen-bonding, which might induce interesting polymer-electrolyte interactions not observed for other side chains.

5.2.1.2 Preparation of Polar PProDOTs

Polymers G2-DMP, G3-DMP, G4-DMP, and BOE-DMP were all prepared by Pd-catalyzed direct hetero(arylation) polymerization (DHAP) by Brandon Ditullio (GT) and Dr. James Ponder (GT). Use of this environmentally benign, tin-free polymerization method is of particular significance, seeing as the resulting polymer must interact with biological systems in its final application, and any trace tin compounds remaining from Stille reactions may be toxic.

In these polymerizations, the brominated DMP unit was coupled with the polar ProDOT comonomers. The synthetic procedures and chemical characterization ($^1$H-NMR, $^{13}$C-NMR, elemental analysis, GPC, etc.) for G3-DMP, BOE-DMP, and the associated monomer precursors can be found in the indicated literature. The synthetic procedures and chemical characterization of the G2-DMP, G4-DMP, and associated monomer precursors can be found in the APPENDIX. An auxiliary batch of G3-DMP “G3-DMP
“BTD-41k)” was also synthesized by the literature methods and compared against the primary batch of G3-DMP used in this work “G3-DMP (JFP-22k).”

Prior to beginning this study, the repeat unit structure was evaluated by $^1$H-NMR, $^{13}$C NMR, and mass spectrometry. The resulting polymers were characterized by $^1$H-NMR, and the chemical purity was confirmed by elemental analysis. GPC-estimated molecular weights relative to PS standards are reported in Table 5.2.1. These $M_n$ estimates are all within the same order of magnitude (13–67 kDa) with $\bar{D}$ values ranging from 1.6–2.5. As approximated, the $M_n$ values are higher for polymers with longer side chains (G4-DMP, BOE-DMP), while polymers with shorter side chains (G2-DMP, G3-DMP) appear to have lower molecular weights. In addition to increasing the repeat unit molecular weight, longer side chains promote enhanced solubility, which allows for longer polymerization time and higher X$_n$, while also increasing the hydrodynamic radius, as the conformational freedom of the side chains promotes solubility and swelling. Combined, all of these factors predictably translate to a larger apparent molecular weight by GPC. As evident from data presented later in this chapter, we observe no obvious or direct dependence of polymer properties on GPC-estimated molecular weight. Thus, we assume any variations in the degree of polymerization are minimal and do not contribute to the overall differences among these materials.

5.2.1.3 Accessing OH-DMP

Polymer OH-DMP was accessed via a post-polymerization thin-film saponification procedure. To obtain OH-DMP, the polymer BOE-DMP was blade-coated or drop-cast from a chloroform solution onto a substrate. The solid film was then immersed in a basic
solution of potassium hydroxide (KOH) and methanol (MeOH). The solution was heated at 55 °C for four hours to hydrolyze the aliphatic esters, as shown in Figure 5.2.2. Neat methanol was periodically added to the hydrolysis solution to maintain the solution level. During the hydrolysis process, a significant amount of white flakey solid accumulated in the methanol solution, which likely corresponded to cleaved side chains leaching from the film and/or precipitation of KOH on the film surface. Upon removal from the basic methanol solution, the film was immersed in a clean solution of methanol, then gently rinsed with methanol and/or DI water.

After saponification, the resulting film showed markedly poor adhesion to the underlying substrate and was prone to delamination. Rinsing with water immediately after

Figure 5.2.2 – Schematic showing blade coating of polymer BOE-DMP and thin film saponification process to access polymer OH-DMP.
hydrolysis seemed to increase propensity of film delamination, perhaps because water is a better solvent for residual KOH or carboxylate left in the film. The nature of the underlying substrate also seemed to influence the extent of delamination, with hydrophobic surface treatments (e.g. dodecylphosphonic acid on glass) resulting in drastically worse film adhesion to the substrate. This effect could be due to a surface energy mismatch and/or blocking of surface oxide sites that potentially could anchor to hydroxyl groups in OH-DMP and stabilize the polymer.

Adhesion was enhanced for films coated on ITO/glass substrates relative to bare glass and polished Si. The differences in adhesion between ITO/glass and bare glass were so drastic that a single continuous film cast over a patterned ITO/glass substrate would delaminate along the boundaries of the pattern: film segments coated over the ITO regions remain adhered, while regions cast over glass regions delaminated. This was likely due to the enhanced surface roughness of the ITO, which increases the effective polymer-substrate interfacial area (and therefore Van der Waals adhesion) and changes the continuity of the film. To test this hypothesis, the hydrolysis procedure was also performed using glass substrates that had been treated with a chemical etching agent to enhance the surface roughness of the substrate. Films coated on these etched glass substrates showed slightly improved adhesion, supporting the hypothesis that the surface roughness of the underlying substrate plays a role in the adhesion of OH-DMP.

FT-IR spectra of the neat polymers before and after this thin film saponification process (BOE-DMP and OH-DMP, respectively) show a new broad feature in the region from 3000–3750 cm\(^{-1}\) (Supporting Figure 5.4.1), which is characteristic of an O-H bond stretch. This confirms the formation of alcohol groups in the polymer. The emergence of
modes ranging from 1300–1400 cm\(^{-1}\) in the OH-DMP spectrum could also represent the presence of alcohol groups, as this would be consistent with O-H bending. For OH-DMP, the carbonyl C=O stretch (1730 cm\(^{-1}\)) and the aliphatic sp\(^3\) C-H stretches (~2854 cm\(^{-1}\), 2923 cm\(^{-1}\), and 2951 cm\(^{-1}\)) are substantially decreased relative to the original BOE-DMP, suggesting that most of the ester-linked side chain has been removed. However, the signal from the carbonyl stretch is not completely absent in the OH-DMP spectrum, which points to an incomplete hydrolysis reaction and/or cleaved side chain trapped in the film. Given the variability of the sample and lack of a calibration curve that could be independently confirmed, the exact extent of hydrolysis was not exactly quantified.

Considering these observations, the true chemical structure of OH-DMP material is likely not correctly represented in Figure 5.2.1. Instead, OH-DMP is likely comprised of a polymer with mixed alcohol/ester functionality, perhaps also with appreciable amounts of cleaved side chain (2-butyloctanoic acid) incorporated within. The incomplete conversion of the ester functionality differs from previous work with a similar saponification process, which reported nearly complete conversion of the alcohol to the ester group\(^{131}\). This prior work was performed on slightly different PProDOTs functionalized with linear hexyl side chains, which are considerably smaller and less sterically encumbering than the 2-butyloctyl side chains used in BOE-DMP. This structural difference could contribute to the inefficiency of the hydrolysis reaction in BOE-DMP by blocking the addition of hydroxide to the carbonyl. Moreover, the previously reported films were cast using different procedures and characterized using different FT-IR methods. Combined, all of these factors combined likely contribute to real or perceived differences in the extent of reaction.
Atomic force microscopy (AFM) studies on BOE-DMP and OH-DMP films showed that the hydrolysis process did not significantly compromise film continuity, feature size, or quality. Based on the AFM topographical height maps of both film surfaces, it appears that OH-DMP (the film accessed through the hydrolysis route) has a slightly rougher and more porous topography than the pristine BOE-DMP film (Supporting Figure 5.4.2). This difference, though small, appeared to be consistent across the multiple spots that were images. It is possible that the slight enhancement in surface roughness arose from rearrangement that occurred from swelling with the hydrolyzing solution and/or the diffusion of cleaved side chain out of the film. Presently, it is not entirely clear whether this small difference in nano-scale roughness would influence any other properties of the film. In some cases, conjugated polymer films with enhanced porosity exhibit higher surface area with more accessible redox-active sites. In some instances, “porous” polymer films show faster ion migration, lower charge transfer resistance, and enhanced capacitance.\textsuperscript{440–442} In the case of OH-DMP, it is unclear whether or not this apparent surface “porosity” extends into the bulk of the film, which would likely be necessary for changing any ion transport processes.

The AFM phase images show greater and more varied phase lag for OH-DMP, which indicates that BOE-DMP and OH-DMP have different surface-tips interactions. This may suggest that cleavage of the side chains also causes additional changes in the surface chemistry (and therefore adhesive forces) and/or viscoelastic properties of OH-DMP. Because changes in both surface chemistry and mechanical properties are expected upon side chain hydrolysis, we cannot determine the dominant mechanism of the phase lag without more additional AFM studies.
The saponification of BOE-DMP to OH-DMP was further confirmed by water contact angle measurements, which assessed the surface energy of the films. As shown in Supporting Figure 5.4.3, the water contact angle was significantly lower for OH-DMP than for BOE-DMP, suggesting an overall higher surface energy for the OH-DMP film. This observation is consistent with the expected changes in film chemistry, where the aliphatic groups in BOE-DMP are mostly removed, leaving highly polar alcohol groups in OH-DMP. As will be discussed later, this change in surface energy is thought to play a role in the determining the vastly different aqueous redox of OH-DMP and BOE-DMP. When compared to an EG-functionalized analogue, the water contact angle of OH-DMP is similar to that of G3-DMP, indicating that similar surface energies can be achieved with the alcohol and glycol functionality (Supporting Figure 5.4.3).

Upon conversion of BOE-DMP to OH-DMP, the hydrolysis procedure is also associated with a partial doping of the π system. This is evidenced by the UV-Vis-NIR absorption spectrum, which shows residual absorption in the NIR for OH-DMP that is characteristic of charge carriers (Supporting Figure 5.4.4). The partially doped film of OH-DMP can be electrochemically restored to its neutral state with only a small amount of trapped charging.

5.2.2 Electrochemical Properties

5.2.2.1 Basic Voltammetric Characterization

To study the aqueous redox activity of the PProDOT films, identical masses of each polymer were deposited onto electrodes and repeatedly electrochemically cycled in a 0.1 M NaCl/H₂O electrolyte. After electrochemical conditioning, cyclic voltammetry (CV)
was performed to evaluate the overall redox characteristics. For each polymer studied, several distinct redox processes were identified, as evidenced by the multiple anodic waves in the CV traces (Figure 5.2.3). The onsets of the first two prominent oxidation processes were determined by DPV studies (Supporting Figure 5.4.6). These values, labeled $E_{\text{ox}} \#1$ and $E_{\text{ox}} \#2$ respectively, are reported in Table 5.2.1.

First, the differences between the electrochemical behavior of BOE-DMP and OH-DMP will be evaluated to demonstrate the effect of side chain hydrolysis on the aqueous redox response. Then, we will compare the properties of all the polar PProDOTs that are show the greatest redox activity in aqueous media—OH-DMP and the EG-functionalized analogues (G2-, G3-, and G4-DMP). This comparison will elucidate the effect of both side chain length and functionality on redox properties.

When comparing the redox response of BOE-DMP and OH-DMP, substantial differences are observed. The conversion of the aliphatic ester side chains in BOE-DMP to the small, polar alcohol groups in OH-DMP results in a notable enhancement in aqueous redox activity. The higher current density in the CV of OH-DMP suggests a greater extent of charge carrier generation and counter-ion uptake in the OH-DMP film. In addition, the $E_{\text{ox}}$ of OH-DMP (-0.38 V) is over 0.60 V lower than that of BOE-DMP (+0.25 V), suggesting that electrochemical doping in aqueous media is substantially more facile in OH-DMP.

For BOE-DMP, the first oxidation process occurring at +0.25 V is quite insignificant; most of the electrochemical doping for this polymer does not begin until much higher potentials of ~0.8 V (Supporting Figure 5.4.6), which is nearing the
electrochemical limit of water. Based on these results, polymer OH-DMP appears to be a promising candidate for aqueous OECTs and other applications where electrochemical interfacing with biological systems is necessary. This result is consistent with findings reported by Pacheo-Moreno et al., who showed that increasing the percentage of alcohol functionality in poly(3-alkylthiophene) derivatives was associated with enhanced aqueous ion transport, which the authors attributed to the greater polarity of the alcohol groups.\textsuperscript{232}

The side chain hydrolysis process yields a material (OH-DMP) that supports the transport of hydrated counter-ions and is capable of repeated electrochemical doping in a saline-based electrolyte. Simply by changing the side chain chemistry, this process transforms a polymer that is redox inactive in aqueous NaCl into a highly redox active material. Even while the de-functionalization process was not entirely efficient, as shown by the FT-IR spectra (Supporting Figure 5.4.1), the transformation was significant enough to substantially change the redox properties of the resulting material. Owing to the short and conformationally restricted alcohol groups in OH-DMP, this material was also found to be insoluble in both water and many common organic solvents (e.g. acetone, toluene, chloroform, hexanes, etc.).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kDa)$^a$</th>
<th>$\bar{D}$</th>
<th>$E_{ox}$ #1 (V)$^b$</th>
<th>$E_{ox}$ #2 (V)$^b$</th>
</tr>
</thead>
</table>

\textbf{Table 5.2.1 – Molecular weight, dispersity, and oxidation onsets ($E_{ox}$, as determined by DPV of drop-cast films in 0.1 M NaCl/H$_2$O) for polar PProDOTs.}
<table>
<thead>
<tr>
<th></th>
<th>Molecular weight determined by GPC (CHCl$_3$, 40 °C) vs. PS standard.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-DMP</td>
<td>-</td>
</tr>
<tr>
<td>G2-DMP</td>
<td>13</td>
</tr>
<tr>
<td>G3-DMP</td>
<td>23</td>
</tr>
<tr>
<td>G4-DMP</td>
<td>67</td>
</tr>
</tbody>
</table>

b) Onsets were extracted from DPV measurements. Potential reported vs. Ag/AgCl reference (single-junction, 3 M aqueous NaCl inner solution).

c) Oxidation wave contributes minimally to overall current response.

Next, we compare the redox properties of all the polar PProDOTs that show the greatest redox activity in aqueous media. These materials include OH-DMP as well as the EG-functionalized analogues (G2-, G3-, and G4-DMP). Comparing the aqueous redox properties of OH-DMP to the polymers with EG-based side chains reveals that the electrochemical behavior of all the materials is relatively similar (Figure 5.2.3B). Each of the polar PProDOTs shows comparable current evolution with applied potential, with at least three discernible oxidation waves occurring within the voltage range tested. As will be evident later in the potential-dependent UV-Vis-NIR absorption spectra, these multiple redox processes do not correspond to distinct, stepwise conversion between neutral, polaronic, and bipolaronic species. Rather, as with polytiophenes, it is thought that the first redox process corresponds to doping of aggregated regions of the polymer film, while subsequent waves arise from oxidation of more torsionally disordered and/or non-aggregated chain segments.\textsuperscript{129,255,257,380}

While the CV characteristics appear to be rather similar, subtle differences in the oxidation onsets of the polymers are evident by DPV (Supporting Figure 5.4.6). As shown
in Table 5.2.1, the polymer with the shortest polar side chains, OH-DMP, shows the lowest principal onset of oxidation ($E_{\text{ox}}$ #1).

Upon first consideration, the low $E_{\text{ox}}$ of OH-DMP could be explained by several possible hypotheses. OH-DMP, having the shortest side chains, may experience less steric hindrance to both interchain interactions as well as intrachain planarization, which would contribute to enhanced stabilization of polaron formation compared to the Gx-DMP polymers. Another possible explanation surrounds differences in the functional group in OH-DMP and Gx-DMP: the hydroxyl functionality in OH-DMP is both a hydrogen bond donor and acceptor, whereas the ether groups in Gx-DMP are only weak hydrogen bond acceptors. Potential differences in hydrogen bonding with the surrounding aqueous milieu may facilitate ion/electrolyte uptake. Lastly, we also consider the possibility that the heated base solution used in the thin film saponification may have annealed the film or contributed to a morphological rearrangement (e.g. enhancing porosity) that resulted in a lower $E_{\text{ox}}$ #1. Given the poor adhesion of OH-DMP to electrodes, we exclude the possibility that the lower $E_{\text{ox}}$ for OH-DMP arises from improved electron transfer kinetics at the polymer-electrode interface.
Figure 5.2.3 – CV traces of A) BOE-DMP and OH-DMP films, and B) polar PProDOT films recorded at 50 mV s\(^{-1}\) in degassed 0.1 M NaCl/H\(_2\)O. Films (initial deposited polymer mass = 16 μg) were drop-cast from solution on GC button electrodes. Current is normalized to electrode area (a = 0.07 cm\(^2\)).
Among the Gx-DMP analogues, increasing the EG side chain length is associated with an increase in $E_{\text{ox}}$, with each additional ethylene oxide unit resulting in a change of approximately +0.10 V (Table 5.2.1). This trend identified in the Gx-DMP series lends credence to the hypothesis that the markedly low $E_{\text{ox}}$ of OH-DMP is predominantly due to its short side chains. In sum, the oxidation potential for these polar PProDOTs tracks roughly with the length of the side chain. The results presented here show that the redox activity of these PProDOTs is limited by side chain length rather than by hydrophilicity. All polymers are sufficiently electron rich and hydrophilic for aqueous redox activity. Instead, the incorporation of such long, electronically insulating side chains increases the first/principal $E_{\text{ox}}$ of the polymer, likely by obstructing interchain interactions and raising the IE.

Contrary to the trend observed for $E_{\text{ox}}$ #1, we find no clear relationship between polymer structure and the second oxidation onset, $E_{\text{ox}}$ #2. If the different oxidation waves in the CV do, in fact, correspond to selective doping of subpopulations with varying extents of order (as has been hypothesized$^{255,257}$), this result would suggest that the redox responses of aggregated and unaggregated domains are governed by different factors.

As explained in CHAPTER 2.3.1, evaluation of the peak current density $i_p$ as a function of CV scan rate $\nu$ can give insight into the relative diffusional limitations of different electrochemical processes. Polymer G3-DMP, with an intermediate side chain length, shows the least diffusion-limited redox characteristics, as it maintains a linear relationships between $i_p$ and $\nu$ for the fastest scan rates (Supporting Figure 5.4.7). In fact, the doping of G3-DMP does not become diffusion-limited until scan rates up to ~1500 mV s$^{-1}$, meaning that G3-DMP films with this particular geometry, electrolyte, and bias
conditions can undergo full (dis)charging in under 1 second. Meanwhile, the scan rate dependence of polymers with shorter and longer side chains, G2-DMP and G4-DMP, deviate from linearity at lower scan rates. Polymer OH-DMP shows redox behavior and scan rate dependence that is most similar to the G2-DMP, which also has relatively short side chains. (Supporting Figure 5.4.7). This trend suggests that there is an optimal intermediate length of glycol side chain length for promoting fast charge transport in the bulk of the polymer film. This is similar to the trend observed for the EG-functionalized polythiophenes (Section 2.2.1, Figure 16), where after a certain length of side chain was achieved, longer polar side chains actually hindered charge transport associated with the electrochemical doping process (Figure 4.2.2).

It should be noted that the lower areal current density and $i_p$ for OH-DMP is likely the consequence of how samples masses were normalized. For the preparation of all films for CV, identical masses of polymers (16 μg) were deposited from solution onto the electrode. Because OH-DMP was accessed through BOE-DMP, the preparation of OH-DMP involved deposited 16 μg of BOE-DMP onto the electrode. Due to the higher side chain mass in BOE-DMP, the electroactive mass of this BOE-DMP film is lower than the analogous 16 μg films of G2-DMP and G3-DMP. Therefore, the resulting OH-DMP polymer also has a lower electroactive mass. Additional small amounts of electroactive mass may have been lost during the hydrolysis process, as well. Therefore, the overall current density for OH-DMP is a bit lower than the other polar PProDOTs.
5.2.2.2 Capacitance

In addition to the general redox response of these polymers, the electrochemical charge storage capacity is thought to be an important parameter for benchmarking OECT active materials. This concept was introduced in CHAPTER 1.3.2 and further expanded upon in CHAPTER 2.3.4.4. To quantify the C* of the polar PPProDOTs studied in this chapter, electrochemical impedance spectroscopy (EIS) was performed on planar films cast on ITO/glass substrates. A range of DC offsets were used to study the potential-dependent properties of the polymers in degassed 0.1 M aqueous NaCl. All films were blade coated from solution onto the electrodes to ensure uniform thickness, except for G2-DMP, which was spray-cast due to poor solubility. The extraction of C* was performed by fitting the low-frequency impedance spectrum to a modified Randles circuit, as described in CHAPTER 2.3.4. Additional experimental details regarding substrate preparation, film casting, and EIS measurements can be found in CHAPTER 2 and CHAPTER 5.5.

The evolution of the potential-dependent volumetric C* for the PPProDOTs roughly corresponds to the i-V trace in the CV (Figure 5.2.4), as expected. Meaningful capacitive behavior was observed for all polar PPProDOTs, beginning around the E\text{ox} of each material and following the shape of the CV trace. As expected, the conversion of polymer BOE-DMP to OH-DMP results in a substantial increase in C* across all potential windows tested (Supporting Figure 5.4.5). In the case of BOE-DMP, the long aliphatic side chains hinder film hydration and ion transport, resulting in low C*. Meanwhile, the polarity of OH-DMP facilitates electrolyte uptake, which contributes to charge carrier stabilization and enhances redox activity.
When comparing OH-DMP to the Gx-DMP polymers, which show similar redox activity in aqueous media (Figure 5.2.3), OH-DMP shows the highest C\(^*\) across the potential range (Figure 5.2.4). The volumetric capacitance of OH-DMP peaks around 106 ± 7 F cm\(^{-3}\) (at +0.4 V vs. Ag/AgCl), while the materials in the Gx-DMP series show peak C\(^*\) ranging from 80–90 F cm\(^{-3}\).

Figure 5.2.4 – Average potential-dependent volumetric capacitance (C\(^*\)) for polar PProDOT films measured in a degassed electrolyte of 0.1 M NaCl/H\(_2\)O. Capacitance was determined by EIS and normalized to the volume of the dry de-doped film. Error bars represent standard deviation of C\(^*\) measurements performed on 3+ different films, cast and measured separately.

While adding long, EG-based side chains is a common approach for conferring aqueous redox activity in conjugated polymers, this result shows that these EG side chains
are not necessary for accessing high-C* materials. Here, we see that small hydroxyl-based side chains can enhance the C* beyond that of glycolated analogues. Evidently, similar and even superior properties can be achieved by using a highly electron-rich backbone (e.g. PProDOT) alongside very small, polar side chains. Decades worth of studies on unsubstituted electropolymerized CPs (e.g. PEDOT, PPy) in aqueous media have established that polar side chains, while not always necessary for aqueous media, do help promote aqueous ion uptake in many cases.\textsuperscript{228,443} Here we see that adding small hydroxyl-based polar side chains can yield properties that are better than longer EG-based polar side chains.

For all polymers in the Gx-DMP series, the C* values evolve with similar magnitudes and potential dependence (Figure 5.2.4). Within the range studied, the capacitance of the EG-functionalized PProDOTs is insensitive to length of the glycol-based side chain. This result is markedly different than the trend identified for the polar PTs studied in \textit{CHAPTER 4}, which showed a substantial change in C* with varying side chain length.

In PProDOTs, the invariance of C* with the EG side chain length provides opportunities for the preparation of versatile active materials. Without compromising performance, the solubility of the material can be enhanced through the incorporation of longer EG-based side chains, as in G4-DMP. This increased solubility is not only advantageous for processing, but it also allows for the synthesis of higher molecular weight materials with a greater degree of polymerization—which potentially could even exceed the critical molecular weight for entanglements, giving rise to different swelling behavior. This could possibly provide interesting opportunities for studying the effects polymer
morphology and macromolecular superstructure on important electrochemical properties (ion transport, actuation, etc.).

5.2.2.3 Redox Stability

As mentioned before, PXDOTs are typically thought to offer enhanced stability in electrochemical applications, as the disubstitution of the thiophene β position provides steric protection against nucleophilic attack on the π-conjugated backbone. As a representative test of stability, a spray-cast film of G3-DMP was cycled 1,000 times by applying two-second square wave pulses from -0.8 to +0.8 V vs. Ag/AgCl in 0.5 M NaCl/H2O. Every 100 cycles, a CV was recorded at (ν = 50 mV s⁻¹) to simulate repeated (de)doping in an OECT device. The CVs and cumulative charge passed for each cycle are shown in Figure 5.2.5.

During extended cycling, the current-voltage response undergoes a gradual change characterized by a merging of the two oxidation peaks into a single broad peak and a slight lowering of the E_{ox}. The lowering of E_{ox} may be attributed to either increased molecular-scale aggregation or an overall change in morphology to a more hydrated structure enriched with electrolyte—either of which could potentially facilitate electrochemical doping. Without further experimentation, the origin of the shifted E_{ox} cannot be unambiguously discerned.

The merging of the two oxidation waves upon long-term cycling could represent either: (i) increasing repulsive interactions between redox sites, resulting in voltammetric broadening of both waves into a single, merged CV feature, or (ii) an overall homogenization of film morphology (at a very small length scale) resulting in a single
broad CV peak. Without more information, neither possibility can be conclusively supported. However, we posit that option (ii) is more, seeing as existing literature suggests that repeat ion infiltration changes of polymer conformation and film structure,\textsuperscript{415} while option (i) is less supported by literature precedent.

Figure 5.2.5 – Superimposed CV traces of G3-DMP performed on spray-cast films on ITO/glass in 0.5 M NaCl/H\textsubscript{2}O from cycle 1 (black) to 1000 (light blue). The cumulative charge passed is shown as a function of number of redox cycles.

Despite these changes, the charge capacity of the polymer film remained fairly constant over 1,000 full doping/de-doping cycles, demonstrating that the electroactivity of
G3-DMP is not compromised much. These results show that this material is a robust platform for aqueous-based electrochemical and bioelectronic devices.

Compared to the stability observed for p(g3T2-T) in 0.1 M NaCl (reported in CHAPTER 2), the stability of G3-DMP in 0.5 M NaCl is similar (Supporting Figure 5.4.8A). It is important to note that the film preparation method, electrolyte concentration, and testing conditions for these measurements are slightly different. With an increased concentration of NaCl in the electrolyte, nucleophilic attack of G3-DMP may be more likely, although the chloride ion is generally not regarded as a very good nucleophile. However, repeating this experiment in 0.1 M NaCl/H\textsubscript{2}O results in no improvement in stability for G3-DMP (in fact, the stability is worsened). Because these experiments were performed approximately 1 year apart, it is possible that the polymer solid underwent initial stages of degradation during this time, which contributed to its reduced redox stability.

Regardless, given the literature on redox stability in polyheterocycles, the difference in stability between the PProDOT (G3-DMP) and the PT (p(g3T2-T)) are not nearly as substantial as expected. This result is similar to the PT stability trend identified in CHAPTER 4, which also showed that additional “open” β positions in the thiophene ring do not necessarily result in worsened stability. It is possible that microstructure and/or swelling play a role in these stability differences. One could envisage that a more ordered material, such as the PT, could stabilize charges to a greater extent or perhaps minimize the infiltration of potential nucleophiles by virtue of its more tightly packed microstructure—both of which would decrease the reactivity of the material to degradative pathways.
Recent studies of PEDOT:PSS have shown that films with increasing crystallinity generally are more stable to repeated electrochemical doping/de-doping. However, in this case, the crystallinity was thought to enhance stability by preventing physical dispersion/delamination of the active layer, rather than by mitigation of some (electro)chemical degradation reaction.

Considering the potential range in these experiments is limited by the relatively small electrochemical window of water, it is also possible that the experiment does not span potentials that are sufficiently high to start seeing differences in so-called “over-oxidation” processes that contribute to PT degradation. Typically, however, these processes occur at potentials outside the electrochemical window of water. Interestingly, the PT analogue also shows a higher C* and overall mass-normalized CV current density than the PProDOT analogue (Supporting Figure 5.4.8B). Despite this higher charge density in the PT, the stability does not seem to suffer. Thus, it is possible that the stability of PTs is not as much of an issue for aqueous applications, where the potential range is already limited by the choice of electrolyte.

5.2.3 Optical Properties

Following electrochemical characterization, the UV-Vis-NIR absorbance spectra of the PProDOT films were monitored as a function of applied electrochemical potential. Films were cast onto ITO/glass electrodes via blade coating, except for G2-DMP, which was spray-coated due to its low solubility. To understand whether these processing differences would introduce complications into the interpretation of the absorption spectra, spray- and blade-coated films of G3-DMP were studied. After electrochemical
conditioning in the aqueous electrolyte, no notable differences were observed in the absorption energy or line shapes of the de-doped films (Supporting Figure 5.4.10). Accordingly, we assume that the differences in the absorption spectra of G2-DMP and the other materials is not the different processing routes used to access these materials.

5.2.3.1 Consequences of Side Chain Cleavage

As described earlier, the polymer OH-DMP was obtained through a thin-film saponification of a BOE-DMP film blade-coated on the ITO/glass electrode. The absorption spectra of the films were recorded in 0.1 M NaCl/H₂O. As shown in Supporting Figure 5.4.4, removal of the side chain density in BOE-DMP material results in an overall red-shifting of the neutral absorption spectrum. However, we note that comparison of the absorption of pristine BOE-DMP and electrochemically conditioned OH-DMP (as done in Supporting Figure 5.4.4) is not entirely valid, seeing as the electrochemical conditioning process in itself can cause a red-shifting of the absorption spectrum in and of itself. The inability of BOE-DMP to fully and reversibly dope/de-doped in aqueous media precludes any comparison of the absorption spectra of these materials in the aqueous electrolyte (see Supporting Figure 5.4.9A, which shows significant charge trapping when attempting to de-dope BOE-DMP).

To better compare the optical signatures of these two materials, BOE-DMP was electrochemically conditioned in an organic electrolyte (0.5 M TBAPF₆/PC). The absorption spectrum of BOE-DMP in its de-doped state was recorded in this environment. As shown in Supporting Figure 5.4.9, the electrochemical conditioning of BOE-DMP does indeed result in a red-shifting of the absorption spectrum, as expected. Comparison of the
conditioned spectra of OH-DMP and BOE-DMP show marked differences, with the OH-DMP spectrum having an enhanced relative contribution of the low-energy feature in the absorption spectrum, which here we attribute to the 0-0 vibronic transition, or A_{0-0} (Supporting Figure 5.4.9). In the context of the hybrid HJ aggregate model, which is commonly used to quantitatively understand the absorption line shape of P3HT, such an enhanced ratio of the absorption intensity of the two principal vibronic transitions (A_{0-0}/A_{0-1}) is associated with increasing interchain coherence, chain planarity, and conjugation length. While it is not entirely clear how rigorously this treatment would apply to PProDOTs, such an interpretation would be consistent with the intuitive expectation that the lower side chain density in OH-DMP facilitates chain planarization and promotes longer conjugation lengths.

5.2.3.2 Absorption Spectra of Neutral PProDOTs

Next, we will compare the absorption spectra of all four polar, aqueous-compatible PProDOTs in their de-doped form (OH-DMP, G2-DMP, G3-DMP, and G4-DMP). After casting on ITO/glass, these films were electrochemically conditioned and then de-doped in the aqueous electrolyte. By eye, all conditioned films appear as homogenous, blue-leaning purple films, with little detectable variation in qualitative color. The absorption spectra of the neutral polymers were recorded while applying a de-doping potential of -0.8 V vs. Ag/AgCl, as shown in Figure 5.2.6. The π-Π* transitions for each material show comparable optical gaps and λ_{max} values (~576-578 nm), indicating similar overall optoelectronic properties.
The two polymers with shortest side chains (OH-DMP and G2-DMP) show residual absorption in the NIR, which could arise from minor charge trapping in the de-doped state. Charge trapping may arise an imbalance in the mass transport and carrier transport properties through the depth of the film. Previous work on PXDOTs has shown that polymers with shorter side chains adopt more compact film morphologies, show more limited ion transport, and therefore exhibit greater charge trapping.\textsuperscript{444} Such an explanation is consistent with the large amount of residual trapped charges observed in BOE-DMP, which cannot support facile hydrated ion transport due to its hydrophobic side chains. This hypothesis is similar to descriptions of charge trapping in non-conjugated redox polymers, which are thought to arise from imbalances in electron transport and mass transport capabilities.\textsuperscript{445}

As shown in Figure 5.2.6, the \(\pi-\pi^*\) absorption bands for all polymers have \(A_{0-0}/A_{0-1}\) ratios below unity, much like the absorption spectra of neutral rr-P3HT. In the context of the HJ-aggregate model, this behavior is indicative of a photophysical HJ aggregate that favors H-aggregation, i.e. inter-chain or through-space coupling of electrons.\textsuperscript{387,393}

What differs among the polymers is the breadth of their absorption spectra. The UV-Vis absorption spectrum of OH-DMP appears to be inhomogeneously broadened, especially into the high-energy region of the spectra range (<550 nm). Commonly, this region is predominantly comprised of contributions from the \(A_{0-2}\) vibronic transition and the absorption of disordered, uncoupled chromophores. The increased low-energy absorption in OH-DMP may represent increased disorder arising from incomplete side chain hydrolysis and/or residual side chain trapped in the film. The absorption spectrum of the polymer with the longest side chains, G4-DMP, is similarly broadened due to increased
relative contributions from $A_{0-0}$, $A_{0-2}$, and high-energy absorbing chromophores. The polymer with intermediately sized EG-based side chains, G3-DMP, has a strikingly narrow absorption spectrum with a suppressed $A_{0-0}$ and $A_{0-2}$.

![Absorption Spectra](image)

**Figure 5.2.6** – Superimposed UV-Vis-NIR absorption spectra of polar PProDOTs biased at -0.8 V vs. Ag/AgCl in 0.1 M NaCl/H$_2$O, labeling 0-0 and 0-1 transitions.

Interestingly, a second batch of this G3-DMP with a slightly higher molecular weight shows an enhanced contribution of $A_{0-2}$ (Supporting Figure 5.4.12). It is also possible that these two batches were synthesized with different extents of incidental homocoupling during DHAP, which would result in an enrichment of the DMP unit beyond.
the 1:1 comonomer ratio. Such a possibility, which is not unfounded even when using the same catalyst loading,\textsuperscript{446} may also result in differences between in the absorption spectra of the two batches. Further studies are needed to understand the origin of the spectral differences between these two batches.

As evident in Figure 5.2.6, the relative intensity of $A_{0-0}$ transition varies across the polymer series. As explained earlier, the relative intensity of this vibronic transition is diagnostic of the extent and nature of aggregation in the film in the context of the HJ aggregate model, with increasing $A_{0-0}$ representing greater through-bond (intra-chain) interactions, increased exciton delocalization (decreased exciton bandwidth), and a higher fraction of aggregates.$^{388,393}$ For the polar PProDOTs studied in this chapter, there is no clear trend with side chain length or polarity in determining the relative intensity of $A_{0-0}$. The $A_{0-0}/A_{0-1}$ ratio is highest for G4-DMP and G2-DMP, while it appears to be slightly lower for G3-DMP. Assuming that these materials behave as photophysical aggregates (which is presently not entirely clear), this would suggest that the side chain may influence the HJ aggregate balance in this system, with G3-DMP being associated with the largest extent of inter-chain over intra-chain coupling.

As summarized above, the absorption line shape of these PProDOTs seems to arise from a subtle interplay of polymer structure, molecular weight, and aggregation properties — much like P3HT, but without the same level of scientific precedent and established fundamental understanding. Unfortunately, due to the rather under-studied nature of PProDOTs, few concrete structure-property interrelations can be extracted from the absorption line shape of these materials. While attempts were made to fit the absorption spectra of the PProDOTs to a standard Franck-Condon progression and/or the HJ aggregate
model, it remains unclear how readily such models can be applied to these PProDOTs, if at all. A distinct type of expertise is required to do so in a rigorous manner.

Seeing as the PProDOTs presented here represent new materials that were synthesized for a targeted application, efforts to quantitatively interpret the absorption spectra of the materials were not pursued in this study. Therefore, more fundamental studies are necessary to understand these absorption spectra and describe their line shapes in an appropriate, quantitative manner. Such work would be incredibly valuable for understanding the behavior of new and existing PProDOTs and establishing important materials design principles.

5.2.3.3 Potential-Dependent Absorption Spectra

Because the neutral and charged states of the polymer exhibit unique optical characteristics, the evolution and extent of the electrochemical doping process can be monitored by tracking the potential-dependent UV-Vis-NIR absorption spectra of the films. The results of these spectroelectrochemical studies are shown in Figure 5.2.7.

Generally, the overall bleaching processes for all polymers show very similar characteristics. In the de-doped state (-0.3 V to -0.4 V), the π-π* transition from 450–650 nm is accompanied by trace absorption in the in the NIR at ~800 nm and 1100 nm. During the initial stages of doping (-0.3 V to -0.1 V), the intensities of these two NIR features increase, and the π-π* transition undergoes moderate bleaching. While the origins of the features at ~800 and ~1100 nm are not entirely clear, some of our more recent work has attributed the state at ~800 nm to an intermediate species with charge-transfer character.417
As the potential is increased, the $\pi-\pi^*$ absorbance band further decreases in intensity, and a broad absorption band centered around 930 nm emerges in the NIR. In the conventional description of doping in CPs, this absorbance corresponds to polarons (radical cations) forming along the backbone. Simultaneously, there is growth of absorbance further out into the NIR (>1200 nm). Again, based on conventional descriptions, this low-energy feature corresponds to bipolarons (dication)s whose $\lambda_{\text{max}}$ can be found outside of the measured wavelength range. At higher potentials (+0.2 to +0.7 V), the bipolaronic band continues to grow. At the highest doping level (+0.8 V), there is very minimal absorbance in the visible range, and the absorption spectrum is virtually entirely dominated by charge carriers. This suggests that all four of the polar PProDOTs can be completely doped in the saline electrolyte, as there is little evidence of neutral species remaining. At +0.8 V, the films all appear transparent by eye. Upon reversal of the potential below -0.4 V, the absorbance of the neutral $\pi-\pi^*$ transition can be restored.

In situ electrochemical conductance measurements of G3-DMP in a similar aqueous electrolyte suggest that the polaronic species at 930 nm are responsible for modulating the bulk electrical conductivity of the material. The conductance peaks with the maximal absorbance at 930 nm (ca. +0.4 V), and the conductance begins to drop at potentials where this spectral feature decreases in intensity (Supporting Figure 5.4.13). This result may indicate that the polaronic states correspond to the primary mobile carriers in the system. However, an alternative interpretation of this result also exists. Because the potential of peak conductance (+0.4 V) also represents the peak CV current density and corresponds to state with the maximal co-existence of neutral species, cations, and
dications, one could also argue that the conductance trend in Supporting Figure 5.4.13 is suggestive of mixed-valence redox conduction.$^{58,185,192}$

**Figure 5.2.7** – Potential-dependent UV-Vis-NIR absorption spectra of polar PPProDOT films A) OH-DMP, B) G2-DMP, C) G3-DMP, D) G4-DMP. Films cast on ITO/glass and biased in 0.1 M NaCl/H$_2$O. Potentials are reported vs. Ag/AgCl.

As explained above, the doping process is characterized by a depletion of the $\pi-\pi^*$ transition in the visible range as neutral chain segments are converted to polarons and
bipolarons. When evaluating the $\pi-\pi^*$ transition throughout the entirety of the doping process, it is evident that the line shape and position of the $\pi-\pi^*$ absorption band is also changing as it is bleached. The positions of the A$_{0.0}$ and A$_{0.1}$ bands blue-shift throughout the doping process, as the remaining neutral population becomes increasingly distorted with electrolyte uptake. The energetic difference between the two principal vibronic features A$_{0.0}$ and A$_{0.1}$ decreases by a factor of ~0.8, indicating a relaxation of the C=C double bond in the polymer backbone. This was recently supported by resonance Raman spectroscopy studies performed on G3-DMP during the doping process.$^{417}$

For all the polymers tested, the absorbance ratio between the main two vibronic peaks ($A_{0.0}/A_{0.1}$) increases during the first oxidation wave. A similar evolution of vibronic features has been observed for chemically and electrochemically doped semicrystalline P3HT,$^{196,411,447}$ where the line shape of the UV-Vis absorption spectrum may be used as a diagnostic proxy for studying the nature of HJ aggregation in the film.$^{388,393}$ Thomas et al. attributed the increasing $A_{0.0}/A_{0.1}$ ratio in electrochemically gated P3HT to the preferential doping of H-aggregates in crystalline regions.$^{196}$ This was later supported by similar studies by Harris et al., who reported a consistent description of heterogeneous electrochemical doping related to the HJ aggregation.$^{411}$ These proposed physical pictures are consistent with previously cited studies that hypothesized different populations of chromophores are sequentially doped with increasing potential.$^{255}$

For the polar PProDOTs presented in this work, we consider the additional possibility that the observed changes in the neutral line shape during the first redox process could also be explained by distortions in chain conformation due to ion intercalation or interactions between excitons with nascent polarons. Even in the case of preferential
doping of specific film domains or regions, electrolyte uptake within and around doped regions may influence the conformation of neighboring neutral domains, resulting in notable changes in the absorption line shape. In other words, chain segments that are not oxidized during this first redox process do not necessarily remain unaffected by electrolyte uptake and charge formation occurring elsewhere in the film. Therefore, without additional data, we cannot definitively conclude that the changes in the vibronic structure with potential are the result of the preferential, stepwise doping of film domains with distinct aggregation characteristics.

At higher potentials (above +0.3 V), the absorption spectra of the remaining neutral chromophores lose all discernible fine structure and becomes increasingly blue-shifted, suggesting that these chain segments are distorted and/or unaggregated. The apparent distortion of these chain segments is consistent with the higher oxidation potential required to dope these populations.

Across the DMP polymer series, the potential-dependent UV-Vis-NIR spectra are all similar. We have already established that the polymers have slightly different oxidation onsets and CV characteristics, and for the most part, the spectroelectrochemical studies reflect these differences. For instance, polymer G2-DMP undergoes more of a spectral change by +0.10 V than G4-DMP due to its lower oxidation onset.

When comparing the charge carrier bands, a few differences can be observed. The origin and implication of these differences in charge carrier absorption are not entirely evident. For instance, the polaron absorption bands seem to peak at very similar wavelengths (920 – 940 nm), with no clear trend based on side chain length. The relative
intensities of the peak polaronic absorbance certainly seem to be different, with the polaron of G3-DMP showing a lower relative absorbance and OH-DMP and G4-DMP showing more intense polaron absorption. However, as explained in CHAPTER 4.2.3 for the PTs, it is not clear what governs the intensity of the polaron absorption, and it is likely depends on a number of factors.

Other differences in charge carrier absorption can be observed when comparing the spectra of the polymers in the highest oxidation states (+0.8 V). At this potential, the spectrum of polymer OH-DMP seems to have contributions from both polarons and bipolarons, as evidenced by the broad and intense absorption spanning from 800–1300 nm. Meanwhile, the spectra of polymers G2-, G3-, and G4-DMP only show evidence of bipolaronic carriers (>1200 nm), with minimal polaronic absorption from 800–1000 nm. So, while OH-DMP has the lowest oxidation onset of all the PProDOTs, the absorption spectra suggest that this material cannot be completely doped to its bipolaronic state. This may be due to a variety of factors, such as the presence of incompletely cleaved side chains which may prevent full doping, or perhaps a limitation in the ability of the polymer to geometrically reorganize and accommodate bipolaronic states.

The bipolaron band of OH-DMP at +0.8 V also seems to be slightly blue-shifted relative to the bipolaron bands of G2-, G3-, and G4-DMP. Because the experimental wavelength range was limited to 1400 nm by NIR absorption of the electrolyte, we cannot unambiguously identify the $\lambda_{\text{max}}$ of the bipolaron. However, at the long wavelength limit of 1400 nm, the bipolaron band of OH-DMP shows a greater intensity, lower slope, and negative concavity when compared to the bipolaron bands of the Gx-DMP series. This may
indicate that the bipolarons are more localized in OH-DMP than they are in the Gx-DMP series.

Some experimental and theoretical studies of chemically doped semicrystalline P3HT have shown that closer “docking” of counter ions to the polymer backbone results in enhanced coulombic interactions and greater localization of the charge carrier.\(^{319,395,448}\) Meanwhile, studies of electrochemically doped PTs suggest that ion uptake predominantly occurs in amorphous regions at low doping levels.\(^{196,401,411}\) At high doping levels, ions penetrate into crystallites and expand lamellar spacing, indicating that counter ions preferentially reside in side chain-rich regions.\(^{196,411,414,415}\) Considering these results, it is interesting to speculate how ions are distributed in a film like OH-DMP, which has minimal side chain density. It is possible that the lack of side chain density in OH-DMP could allow counterions to dock closer to the \(\pi\)-conjugated backbone, which would increase the electrostatic attraction between the ion and charge carrier. This would contribute to greater polaron localization, potentially accounting for the seemingly blue-shifted bipolaron band. If this hypothesis were true, however, it is not clear why the polaron band OH-DMP is not similarly blue-shifted.

Further work is required to determine the origin of the differences in the charge carrier absorption bands and understand how side chain length potentially could influence counterion distance and charge pinning. Presently, the spectroelectrochemical studies simply demonstrate that the polar PProDOTs can all be doped in aqueous media. At a very high level, the doping proceeds in a similar fashion.

5.2.4 Thin Film Microstructure
The factors governing charge carrier generation, stabilization, and transport in conjugated polymers are complex and often depend on a range of interrelated chemical, electronic, and structural properties. For neat polymer films in the solid state, the macromolecular arrangement of chain segments is known to play a critical role in shaping the optoelectronic properties of the bulk material. As explained before, it is currently not known what type of solid-state, long-range order (if any) is desirable for OECT applications. Therefore, exploratory X-ray studies were performed in a cursory manner to understand the extent of ordering in the PProDOT films.

Grazing-incidence wide angle X-ray scattering (GIWAXS) was performed on neat PProDOT films cast on Si wafers. All polymers were blade coated from chloroform solutions, except for G2-DMP. Due to the poor solubility of G2-DMP, this material could not be dissolved at the concentrations required to fabricate comparable films by blade coating. Accordingly, GIWAXS samples of G2-DMP were spray-cast from dilute chloroform solutions. Certainly, the casting method can have a significant impact on how conjugated polymers arrange in the solid state. However, in these particular PProDOT films, the microstructure does not seem to depend much on the processing method. The scattering patterns of spray- and blade-coated films of polymer G3-DMP are strikingly similar (Supporting Figure 5.4.14). For G2-DMP, spin-coating and spray-coating from chloroform yields identical scattering patterns (Supporting Figure 5.4.15). Therefore, we assume that processing effects are minimal, especially because the processing solvent, film thicknesses, and solution ages were identical.
Figure 5.2.8 – Representative GIWAXS patterns for polar PProDOTs films. Casting method is indicated in white text: A) OH-DMP, with detector artifact shown as a red line, B) G2-DMP, C) G3-DMP, and D) G4-DMP. For panels B-D, intensities are normalized to film thickness as measured by a profilometer. Scattering intensities are represented linearly on a purple-red color scale. Not that the absolute scattering intensity for panel A cannot be compared to B-D, as this sample was analyzed at a different beamline.

The two-dimensional GIWAXS diffraction patterns of the PProDOT films do not suggest the presence of any significant crystalline microstructure or long-range order (Figure 5.2.8). The diffracting regions of the film exhibits a slight face-on texturing relative
to the substrate, as indicated by the notable out-of-plane ($q_z$) scattering around $q \approx 1.6 \, \text{Å}^{-1}$, which we tentatively assign to scattering from disordered, low-coherence π stacks (020). All polymers have similar π stacking distances considering the standard error of the measurement ($d_{020} = 4.0 \, \text{Å}$, Table 5.2.2). This feature, which we attribute to weak scattering from π stacking, is superimposed on a broad, amorphous scattering halo which is commonly attributed to side chain disorder in alkyl-functionalized polythiophenes. It should be noted that this assignment is tentative and further studies are required to confirm the identity of this peak.

Scattering in the $q_z$ direction at low $q$ (0.3–0.4 Å$^{-1}$) is attributed to the lamellar stacking (100) direction and corresponds to the distance between adjacent polymer chains. Across the Gx-DMP series, the lamellar stacking moderately increases with the length of the side chain by approximately 1-2 Å per additional ethylene oxide unit. Seeing as the length of one ethylene oxide repeat in PEO unit is approximately 3.5 Å (depending on the conformation/solvation), this change in $d_{100}$ is a bit smaller than anticipated, likely due to the side chain tilt angle and/or conformational differences in the solid state. OH-DMP shows the smallest lamellar spacing, which likely arises from the reduced side chain length.

Scattering patterns of BOE-DMP, the ester precursor to OH-DMP, shows a broad isotropic scattering feature $q \approx 1.4 \, \text{Å}^{-1}$ (Supporting Figure 5.4.16). This arc corresponds to lattice spacing that is a bit larger normal π stacking. Accordingly, we attribute this to the “amorphous halo” thought to arise from side chain interactions and do not identify any scattering from π stacks.
Conversion of BOE-DMP to OH-DMP is associated with the emergence of a prominent peak at higher q in the out-of-plane direction \((q_z \approx 1.6 \ \text{Å}^{-1})\), which we speculatively attribute to possible \(\pi\) stacking that results as side chain bulk is removed from the film. However, further studies would need to be performed to prove this. Upon side chain removal, the lamellar spacing decreases from 21.4 Å in BOE-DMP to 15.0 Å in OH-DMP (Table 5.2.2). The magnitude of the lamellar spacing in OH-DMP is a bit larger than what may be anticipated considering the side of the propylene bridge and side chains combined. Without further studies, we cannot definitively understand why the OH-DMP has a lamellar spacing 15.0 Å. However, we speculate that this could be attributed to the presence of un-cleaved side chains expanding the lamellar structure and/or increased void volume in the film.

Because the GIWAXS pattern of OH-DMP was collected on a different instrument than the other films, the absolute magnitude of the scattering intensities cannot be compared. Instead, comparing the relative intensities of corresponding peaks within patterns may provide information about microstructural changes. In OH-DMP, the broad halo thought to arise from “side chain interactions” is suppressed relative its prominence in BOE-DMP. While this could possibly be the result of side chain removal, we again emphasize the cursory nature of these GIWAXS studies. To unambiguously assign and understand the relatively weak scattering observed for these films, more thorough experimentation, analysis, and theoretical treatment would be required, which is presently outside the scope of this work.
Table 5.2.2 – Speculated lattice parameters corresponding to the π-π stacking distance, $d_{(020)}$, and lamellar spacing distance, $d_{(100)}$, for PProDOT films. Parameters extracted from scattering in out-of-plane ($q_z$) direction, unless otherwise noted.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Casting Method</th>
<th>$d_{(020)}$ (Å)</th>
<th>$d_{(100)}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOE-DMP$^a$</td>
<td>Blade</td>
<td>--</td>
<td>24.1</td>
</tr>
<tr>
<td>OH-DMP$^b$</td>
<td>Blade</td>
<td>4.0</td>
<td>15.0</td>
</tr>
<tr>
<td>G2-DMP$^c$</td>
<td>Spray</td>
<td>4.0</td>
<td>21.0</td>
</tr>
<tr>
<td>G3-DMP</td>
<td>Blade</td>
<td>4.0</td>
<td>22.5</td>
</tr>
<tr>
<td>G4-DMP</td>
<td>Blade</td>
<td>4.0</td>
<td>24.3</td>
</tr>
</tbody>
</table>

$^a$ Scattering pattern available in Supporting Figure 5.4.16.
$^b$ GIWAXS data collected at a different beamline.
$^c$ Spray-cast due to low solubility.

Note: All values represent average distances calculated from two separate films, cast and measured separately. Std. err. < 0.1 Å.

The extent of disorder in any given crystallographic direction can be quantified by the paracrystallinity parameter, $g^*$, which encompasses static fluctuations around a given lattice spacing. Here, we find the $g^*$ values for the polar PProDOTs (OH-, G2-, G3-, and G4-DMP) to be approximately 20% in the $(0k0)$ direction. This indicates an amorphous film microstructure and suggests that the intermolecular order associated with π-stacks is not maintained for an appreciable length scale. For comparison, semicrystalline rr-P3HT typically exhibits relatively tighter π-stacking distances ($d_{(020)} \approx 3.8$ Å) as well as much lower paracrystallinity in the $(0k0)$ direction ($g^* = 4-7\%$, depending on molecular weight and processing conditions), indicating significantly less disorder in the system.
The 2D GIWAXS pattern of the polar PProDOTs appears to be more consistent with short-range, weakly diffracting aggregates. Aggregates, which are distinct from crystallites, are comprised of chain segments that exhibit order in only one dimension (e.g. π-stacking) without participating in strong order along complementary crystallographic directions (e.g. lamellar ordering). Duong, Toney, and Salleo\textsuperscript{315} provide an excellent comparison of aggregates and crystallites. For the polar PProDOTs studied in this work, such aggregation is apparent from the scattering patterns, which show weak out-of-plane π-π scattering features that are not complemented by any in-plane lamellar structures of similar scattering intensity. While aggregates are necessary for the formation of bulk crystallites, they may also exist in amorphous matrices. Notably, only aggregates with sufficient coherence are detectable by GIWAXS. The GIWAXS patterns and sine-corrected line cuts suggest that PProDOTs, unlike many widely studied conjugated polymers, do not assemble into domains with intermolecular order spanning multiple dimensions. Rather, we see that any ordering of chain segments in these materials is incredibly short range and confined to one dimension only.

Accordingly, X-ray methods like GIWAXS are not expected to be particularly useful for studying the properties of the pristine PProDOT films. These materials are predominantly amorphous in the as-cast state. If substantial ordering is induced by doping, as has been shown to occur for other materials,\textsuperscript{135,320,414} a more useful comparison may be possible by evaluating the scattering patterns of the films in their electrochemically conditioned states. However, considering that X-ray methods will predominantly probe regions with enough coherence for appreciable diffraction, it is important to note that these
methods would still fail to characterize amorphous domains of the film—which also play a substantial role in the redox process, especially when it comes to regulating ion transport.

### 5.2.5 OECT Devices

Following the materials characterization efforts described above, the next steps of this study involved incorporating these polar PProDOTs in aqueous-based OECTs, testing their utility in such devices, and comparing the associated device performance.

#### 5.2.5.1 Proof-of-Concept Device with G3-DMP

First, to demonstrate the functionality of PProDOTs in aqueous OECTs, one of the polar PProDOTs was chosen for testing in a conventional OECT device configuration. The polymer G3-DMP was incorporated into OECT devices that were fabricated and tested by Professor Jonathan Rivnay (NU). These devices consisted of gold source and drain contacts, parylene passivation layers, along with rectangular channels. Details concerning device fabrication can be found in the literature.\(^{227,324,401}\) OECT devices with these simple rectangular channel geometries are sometimes referred to as planar OECTs, or pOECTs.\(^{451}\) Such pOECTs are distinct from OECTs fabricated on interdigitated electrodes (iOECTs), which consist of a comb-like channel geometry and usually have higher W/L ratios.

G3-DMP was blade coated onto the pOECT substrates provided by Prof. Rivnay, and the channel patterned through a mechanical lift-off of a sacrificial parylene layer, as described in the literature.\(^{324}\) The device was tested using a conventional common-source configuration (as described in CHAPTER 2.6.1), with a 0.1 M NaCl electrolyte and a Ag/AgCl pellet as the gate electrode.
OECT device characteristics (Figure 5.2.9) show reversible doping/de-doping of G3-DMP, accumulation mode operation, and minimal hysteresis. The maximum measured transconductance (622 µS) occurs at $V_G = -0.7$ V. The OECT device shows an on/off current ratio ($I_{ON/OFF}$) exceeding $10^5$, demonstrating an impressive conductivity amplification in the channel rivaling devices fabricated with other state-of-the-art active materials.\textsuperscript{194,203,416} This study represents the first use of a PProDOT-based channel in a saline-based OECT and the first aqueous-compatible OECT active materials synthesized by DHAP. Since reporting G3-DMP in 2018,\textsuperscript{227} other groups have also started to use DHAP for synthesizing accumulation-mode OECT active materials,\textsuperscript{452} demonstrating the impact of this work on the field.

Figure 5.2.9 – Planar OECT characteristics for a device fabricated with G3-DMP. A) Transfer curve with corresponding transconductance ($g_m$) $V_D = -0.5$ V. B) Output curves for gate voltages ranging from $+0.10$ V to $-0.80$ V recorded every 0.05 V. Data correspond to a sweep rate of 0.20 V s$^{-1}$ and device with channel dimensions of 50 µm x 50 µm (WxL), a film thickness $d = 282$ nm, and an ambient electrolyte of 0.1 M NaCl in H$_2$O in ambient conditions. Arrows indicate the direction of the sweep. Figure has been adapted with permission from the literature.\textsuperscript{227} © 2018 Wiley-VCH.
The volumetric capacitance \( C^* \) of the blade-coated G3-DMP film was calculated to be 111 F cm\(^{-3} \) at NU. This value was determined by EIS performed on a polymer-coated Au electrode integrated onto the same device substrate. This \( C^* \) value is slightly above the EIS-derived peak \( C^* \) calculated at Georgia Tech (~80 F cm\(^{-3} \), Figure 5.2.4). The discrepancy may be the result of differences in AC bias used for the EIS measurement (10 vs. 5 mV), the circuit fitting (C vs. CPE), the electrode configuration (two- vs. three-electrode), electrode-dependent film properties (gold vs. ITO), thickness measurement procedures, and/or a number of other causes. Regardless, both of these \( C^* \) values for G3-DMP are comparable to that of many PEDOT:PSS-based active materials.\(^{201} \) Based on measurements performed by collaborators at NU, the apparent hole mobility (\( \mu \)) of G3-DMP in the OECT device was measured to be 0.063 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at \( V_G = -0.6 \) V. This value was calculated from an impedance-based bandwidth matching technique\(^{325} \) used to extract the hole transit time in the channel.

Assuming commonly accepted descriptions of OECT device behavior are correct, the product of \( \mu \) and \( C^* \) can be regarded as a system-level figure of merit for OECT active materials.\(^{201} \) The decoupled values of \( \mu \) and \( C^* \) for G3-DMP, as measured in the context of this study, are plotted in Figure 5.2.10. The \( \mu \) and \( C^* \) values for other high-performing p-type OECT active materials, as adapted from the literature,\(^{201} \) are also plotted in Figure 5.2.10 as a comparison. The purported figure-of-merit (the \( \mu C^* \) product), increases along the diagonal of the plot. Based on this comparison, the G3-DMP device out-performs a number of state-of-the-art active materials in terms of both \( \mu \) and \( C^* \). The G3-DMP device is also within range of the higher-performing devices made with other materials, shown in Figure 5.2.10. In fact, the results collected for this study indicate that G3-DMP is the
highest performing accumulation mode PXDOT-based active material reported to date, even for the unoptimized measurement reported in this study.

![Graph showing volumetric capacitance C* vs. mobility μ for p-type or ambipolar OECT materials as tested in pOECTs under similar conditions. The C* and μ of G3-DMP (purple star) is shown relative to the state-of-the-art p-type materials, including glycolated polythiophenes/polythienothiophenes (PT/PTT, yellow triangles), PEDOT-based systems (PEDOT, blue circles), a glycolated BTD derivative (BDT, green diamond), and a thiophene-based polyelectrolyte (PTH, magenta square). All literature values for μ and C* for these reference materials were adapted from Inal et al. This figure has been adapted with permission from the literature and modified for clarity. © 2018 Wiley-VCH.]

It is important to note several considerations when considering the pOECT results presented above. First, the device characteristics correspond to a single device. Accordingly, no geometry scaling measurements were performed to rigorously confirm the relationship between the device parameters. Secondly, as explained before, comparisons
of material performance are based on a widely accepted model.\textsuperscript{175-199,201} Possible limitations to this model are briefly outlined in CHAPTER 1.3.2 and CHAPTER 2.

5.2.5.2 Interdigitated OECTs

The promising results from G3-DMP motivated the testing of the other polar PProDOTs as channel materials in aqueous OECTs. Subsequent devices studies, which were conducted at Georgia Institute of Technology, employed the use of interdigitated S/D electrodes. As opposed to the pOECTs used for the preliminary G3-DMP device studies, which had a rectangular channel, the iOECTs used for the device studies at GT involved two interlaced, comb-like S/D electrodes. As explained earlier, the interdigitated nature of the electrodes give rise to extremely long channel widths (W) with relative source channel lengths (L). Accordingly, iOECTs give higher on currents with greater signal amplification than pOECTs devices of the same overall footprint area. For this reason, iOECTs have been employed to record very small signals, such as cellular action potentials.\textsuperscript{205} Occasionally, such interdigitated electrodes are also used as a platform for proof-of-concept OECT device testing.\textsuperscript{426,428,434,453} \textit{In situ} conductivity measurements also typically use interdigitated electrodes because the high W/L ratio usually results in a greater absolute current signal in response to the relatively small AC biases used to probe transport in such measurements.

For testing the OECT characteristics of the remaining PProDOTs, commercially available iOECTs were obtained and coated with the polymer active layer. These electrodes fit nicely into a complementary electrochemical cell which was purchased from the same supplier. The cell was connected to a test fixture controlled by a parameter analyzer.
comprising two SMUs. A schematic of the iOECT test cell can be found in Figure 2.6.1. Instead of unbuffered 0.1 M NaCl/H$_2$O, which is the most common electrolyte used in OECT testing, a 1× phosphate buffered saline (PBS) solution was employed to mimic physiological conditions and prevent pH variations over extended testing periods. PBS consists of an aqueous solution of 0.137 M NaCl along with a small amount of KCl and phosphate buffers for a fixed pH of 7.4.

The results for the iOECTs fabricated with polymers in the G$_x$-DMP series all yielded similar characteristics, showing p-type accumulation-mode device operation. Representative device characteristics for G2-DMP, G3-DMP, and G4-DMP are presented in Supporting Figure 5.4.17, Supporting Figure 5.4.18, Supporting Figure 5.4.19, respectively. The iOECTs made with G3-DMP appear to show the least amount of hysteresis in the transfer characteristics (Supporting Figure 5.4.18). In principle, such hysteresis may be correlated to the diffusional limitations of the redox process. However, it should be noted that the hysteresis did not change for transfer characteristics collected using low scan rates (~10 mV s$^{-1}$). The hysteresis was also observed when performing similar iOECT measurements in a four-electrode architecture with a proper reference electrode (Supporting Figure 5.4.20). This hysteresis likely arises from the geometric reorganization of the polymer upon electrochemical doping, which stabilizes polaron states and therefore may requires a greater reserve bias to effectuate de-doping.

Assuming that the transconductance ($g_m$) of these OECT devices scales linearly with thickness, as has been proposed for other OECT active materials,\textsuperscript{175,201} these iOECTs devices may be roughly compared by normalizing the apparent $g_m$ to the active layer thickness (d). A comparison of the thickness-normalized $g_m$ for the PProDOT-based
devices is shown in Figure 5.2.11. As evident, all Gx-DMP active layers result in similar normalized $g_m$ values, indicating comparable performance. The standard deviation for these measurements is rather high, which will be discussed later.

Despite exhibiting the largest peak $C^*$, the polymer OH-DMP could not be integrated into robust iOECTs owing to its extremely poor adhesion to interdigitated electrodes. Platinum and gold electrodes with different surface treatments were tested as alternative electrodes, but OH-DMP delaminated from all electrodes upon immersion in water, as explained in CHAPTER 5.2.1.3. So, while side chain cleavage resulted in a film with greatly enhanced $C^*$, this technique had negative ramifications on the physical properties of the polymer, resulting in poor interfacial adhesion and preventing its viability in OECT devices.

Because neat films of OH-DMP could not be incorporated into OECT devices, 20 wt.% (relative to BOE-DMP) of an epoxide-based crosslinking agent was added to the precursor BOE-DMP solution prior to casting. This crosslinking agent, commonly known as GOPS (3-glycidyloxypropyl)trimethoxysilane), is frequently used to prevent the dispersion of PEDOT:PSS in aqueous OECTs. While the mechanism of crosslinking is not entirely known, it is hypothesized that GOPS crosslinks through sulfonate groups on PEDOT:PSS.\footnote{While OH-DMP has no sulfonate groups for crosslinking, it is conceivable that the hydroxyl group in OH-DMP could add to the epoxide in GOPs, thereby participating in the crosslinking process.}

BOE-DMP+GOPS films were cast and heated in air at 140 °C for two hours and then hydrolyzed in 2 M KOH in methanol, as described previously. The resulting film did
not delaminate in water, suggesting that the addition of GOPS helped to stabilize the OH-DMP film. However, devices fabricated with OH-DMP+GOPS mixture performed much worse than the Gx-DMP analogues, showing reduced normalized transconductance values (Figure 5.2.11). In principle, this could be due to the addition of electrochemically inactive GOPS to the film, which would likely lower both C* and μ. Addition of GOPS in similar amounts has been shown to significantly reduce μ of PEDOT:PSS active layers. Adding an inert crosslinking agent to this material defeats the purpose of removing the side chain density from the film. Therefore, this is not a practical or effective route towards high-performance OECT channel materials.

Figure 5.2.11 – Thickness-normalized peak transconductance values for iOECT devices fabricated with PProDOTs operating in 1× PBS with a standard 3-terminal configuration. Error bars represent standard deviation of 3+ device measurements with active layers of different film thicknesses.
As noted previously, the average thickness-normalized $g_m$ for the PProDOT-based iOECTs show extremely high standard deviations that approach 50% of the nominal average (Figure 5.2.11). We attribute this large variation to the fact that these OECTs devices, unlike many others in the literature, do not show a linear dependence of $g_m$ on active layer film thickness (d). Therefore, normalizing $g_m$ by thickness, as done in Figure 5.2.11, does not provide a physically accurate representation of the device characteristics.

Based on the prevailing descriptions of OECT device operation, the thickness-normalized transconductance ($g_m d^{-1}$) should be a single value depending only on the identity of the active material, with a plot of $g_m$ vs. thickness affording a linear relationship.\textsuperscript{175,201} However, for these devices, we do not observe a proportional, linear dependence of $g_m$ on thickness (Figure 5.2.12A). This non-linearity may, in principle, arise from a number of factors, including thickness-dependent microstructure and morphology (as alluded to in CHAPTER 2.3.4.4). In this particular case, we attribute a large part of this non-linearity to over-coating of the interdigitated electrodes with the polymer film. The thickness of the platinum contacts in the interdigitated electrodes is approximately 175 nm, thus the electrode surface is elevated from the insulating surface between the two polymers. Therefore, polymer active layers coated to thickness beyond 175 nm will experience a non-uniform electric field throughout the depth of the film, as illustrated in Figure 5.2.12B. Accordingly, there is likely a thickness dependence of carrier transport, $I_D$, and $g_m$. Among the different film thicknesses tested, the value of $g_m$ seems to saturate once the thickness of the polymer film exceeds that of the platinum electrodes (Figure 5.2.12A).
In the field of non-conjugated redox polymers, this saturation of transport in thicker active layers is used to make fundamental comparisons of inter-site redox hopping in electroactive films. So-called “over-coated electrode” configurations yield a single limiting current that is used to extract a thickness-independent charge transport parameter. These similar observations made in the redox polymer community lend credence to the observation of thickness dependence presented here. We conclude that these overcoating effects may indeed be generalizable to conjugated polymers and potentially convolute scaling relationships in OECTs (as well as in “in situ conductivity” measurements).

In sum, additional work is required to understand the limits of these scaling relationships—both when the active layer is thinner and thicker than the underlying S/D contacts. This holds not only for iOECTs but also for pOECTs, where one may expect the same thickness effects to manifest. Establishing this relationship is critical for understanding the fundamental geometrical restraints of the measurement.
Figure 5.2.12 – A) Peak $g_m$ in iOECTs made with G3-DMP for varying channel thicknesses (d). Error bars for $g_m$ represent standard deviation of 3 different devices and 3 thickness measurements. B) Schematic of IDE set-up adapted from the Khan et al. and re-labeled. © 2015, MDPI. The diagram depicts a bird’s eye view (left) and cross-sectional view (right) of an interdigitated platform used to study transport in a polymer film, showing electric field lines.

5.2.5.3 Comparison of Device Results

As mentioned earlier, the performance of iOECT devices fabricated with Gx-DMP copolymers were similar, exhibiting an $I_{ON/OFF}$ of roughly $10^3$ for each polymer and
averaged normalized transconductance values within error of each other. Notably, this $I_{\text{ON/OFF}}$ ratio is two orders of magnitude lower than that found for pOECTs made with G3-DMP tested at NU.

The disparities in $I_{\text{ON/OFF}}$ likely arise from limitations associated with the geometry associated with the commercially available interdigitated electrodes. Because the active layer was not patterned, a significant portion of the interdigitated platinum fingers are exposed to the polymer without adequate passivation. While this makes device fabrication easier because the active layer is not patterned, this configuration likely raises the $I_{\text{OFF}}$ of the transistor. Even in the de-doped state, there could be some amount of electrolyte in the polymer film that contributes to a measured ionic current.

A second factor that could impact the $I_{\text{ON/OFF}}$ differences is contact resistance. Such contact resistance (called “source-drain series resistance” in some disciplines) does not necessarily arise from the connection between the cell and the metal $S/D$ pads—although this certainly can (and has been shown to) play a substantial role if not mitigated. Rather, the contact resistance in question is associated with carrier injection at the polymer-electrode interface, and it varies for different polymer structures, electrode work functions, and even with the polymer doping level ($V_O$),\textsuperscript{204–206,208} analogously to contact resistance in OFETs.\textsuperscript{212} The combination of the raised $I_{\text{OFF}}$ (arising from incomplete electrode passivation) and the reduced $I_{\text{ON}}$ (arising from contact resistance) yields an overall lower $I_{\text{ON/OFF}}$.

Not only do the $I_{\text{ON/OFF}}$ values differ for the GT and NU devices, but the apparent $\mu C^*$ products extracted from the device characteristics are drastically different. When
accounting for the different geometries and bias conditions, the pOECTs tested at NU yield a $\mu C^*$ that is three orders of magnitude higher than the product for the iOECTs at GT ($\sim$30 vs. $\sim$0.05 F cm$^{-1}$ V$^{-1}$ s$^{-1}$). While we previously highlight limitations associated with normalizing device characteristics (e.g. $g_m$) to active layer thickness, it is unlikely that this 1,000-fold difference in the $\mu C^*$ product can be explained by thickness effects alone, seeing as the film thicknesses in these devices were all within an order of magnitude (200–500 nm). Therefore, this result clearly shows that the device configuration has a significant impact on the apparent system figure-of-merit.

With extremely long effective channel widths and relatively short channel lengths, the series contact resistance in iOECTs can be easily dominated by the channel resistance. The implication of this, which was demonstrated by Lüssem and colleagues, is that transconductance saturates at high W/L channel ratios as contact resistance becomes increasingly influential.$^{204,455}$ Liang et al. conducted a thorough and comprehensive study of scaling effects in iOECTs and showed that the enhanced contribution of contact resistance in iOECTs results in deviations from the expected device characteristics, especially for devices with short channels.$^{205}$ In a recent report comparing the iOECTs and pOECTs made with the same active material, the device $g_m$ was found to scale differently for the two electrode architectures, which the authors attribute to contact resistance effects.$^{456}$ Therefore, while interdigitated electrodes can be useful for demonstrating that a material can or cannot be successfully incorporated into OECTs, they are not good platforms for making performance comparisons, especially when using high-performing channel materials.
For high performing materials that become very conducting when doped, the channel resistance is so small that it can be easily dominated by the contact resistance. The contact resistance, rather than the channel resistance, will then become the limiting property of the device. In fact, iOECTs with the same electrode architecture and two different active materials (G3-DMP and a carboxylic acid-substituted polythiophene) result in identical device characteristics, despite the two materials having otherwise vastly different redox properties. This points to a configuration-based limitation associated with the interdigitated platform.

While contact resistance is most obvious in iOECTs, pOECTs can also suffer from the same pitfalls. In these planar geometries, which are most commonly used in the literature to benchmark systems, contact resistance can also play a role in determining the device characteristics. This highlights the need for more rigorous metrology in materials and device testing now the field has moved past foundational work. By combining experimental results and simulations, Björn Lüssem and colleagues have done excellent work in accounting for contact resistance and geometry effects in OECTs.

Extracting meaningful parameters from OECT data requires careful analysis and minimization of all parasitic capacitances and resistances. Qualitatively, the OECT results presented in this chapter demonstrate that the polar PProDOTs are indeed functional and may be incorporated into aqueous-based OECTs, yielding performance that is similar to devices made with state-of-the-art materials. However, testing and comparing devices in any quantitative manner requires a more thorough analytical process. Such an approach would involve fabricating adequately patterned and passivated devices, exploring different
device architectures and channel geometries, and performing transmission line measurements under different bias conditions to analyze all of the competing processes at play.

5.3 Conclusions

This work explores the structural effects governing the aqueous redox properties of solution-processable, polar-functionalized PPProDOTs. We report a series of electron-rich copolymers, all based on the DMP (2,2-dimethylPPProDOT) unit, that are functionalized with side chains of different size, length, and polarity. This family includes three materials with ethylene glycol (EG)-based side chains of various lengths (G2-, G3-, G4-DMP) as well as ester (BOE-DMP) and hydroxyl-functionalized (OH-DMP) analogues.

Among the PPProDOTs with EG-based side chains (Gx-DMP), we see a modest dependence on the oxidation onset with the length of the side chain. All materials are similarly redox active in saline and can be fully doped to their bipolaronic form within the electrochemical window of water. Additionally, preliminary results suggest that these PPProDOTs are stable in aqueous media, making them promising candidates for OECTs and other bioelectronic devices. Across the Gx-DMP series, we see little influence of side chain length on the volumetric capacitance, overall redox activity, and potential-dependent absorption spectra of the films. Remarkably, this system appears to be insensitive to the length of the EG side chain, allowing for the development of materials which with greater solubility and higher molecular weight (e.g. G4-DMP) without compromising performance. GIWAXS studies show that all materials have similar amorphous microstructures and little
long-range order in their as-cast state, regardless of the side chain length and processing method.

Notably, this result is distinct from the trend identified for PTs in CHAPTER 4, which showed a substantial dependence of redox activity, capacitance, and microstructure on the length of the EG side chain. The trends identified for the PProDOTs and PXDOTs indicates that design rules for OECT active materials are not generalizable across material classes. The positioning of the side chain onto the π-conjugated backbone, whether directly onto the backbone through sp$^2$ hybridized carbons (as in PTs) or further away from the backbone through sp$^3$ hybridized carbons (as in PProDOTs), can influence how sensitive the material is to side chain length. The functionalization pattern used in the PProDOT system seems to yield materials with properties that are overall less sensitive to side chain length.

Next, this work demonstrates how a DMP copolymer with an aliphatic ester side chain (BOE-DMP) can be cleaved through a post-polymerization modification to access a highly polar, alcohol-functionalized polymer (OH-DMP). Through this process, an otherwise hydrophobic polymer with limited electroactivity in water can be transformed into a material with enhanced redox activity in physiologically relevant media. This method, which uses a thin film saponification process, can be leveraged to yield an aqueous-compatible CP with volumetric capacitance values exceeding the EG-functionalized analogues, therefore demonstrating that there are alternative routes towards designing high-performing OECT active materials. To realize the potential of this process in bioelectronic applications, additional effort is required to improve the interfacial adhesion of the active layer to the underlying electrode.
Finally, these PProDOTs were incorporated into aqueous OECTs for device testing. As a preliminary study, G3-DMP was incorporated as a channel material into a planar OECT device geometry, yielding devices that out-perform many PEDOT:PSS-based OECTs and rival some of the state-of-the-art systems. The remaining polar PProDOTs were incorporated into interdigitated OECTs with a PBS electrolyte. Interdigitated OECTs fabricated with the EG-functionalized PProDOTs materials show comparable transconductance values and on/off drain current ratios, suggesting similar performance when tested in this particular device geometry. However, the characteristics of the interdigitated devices point to a configurational issue that limits meaningful data. The results from these studies highlights the important role of electrode architecture on device performance.

More rigorous and controlled measurements accounting for device architecture, electrode geometry, and contact resistance are required to draw any significant conclusions about PProDOT-based OECTs.
5.4 Supporting Figures

Supporting Figure 5.4.1 – FT-IR spectra of solid samples of BOE-DMP and OH-DMP, highlighting hydroxyl (O-H), aliphatic (sp\(^3\) C-H), and carbonyl (C=O) stretches.
Supporting Figure 5.4.2 – AFM height (left) and phase (right) images for A) BOE-DMP and B) OH-DMP blade coated on Si wafers. Imaging was done on dry films in standard tapping-mode (~150 kHz). $R_q$ represents the root-mean-square roughness averaged from three different 500 nm x 500 nm square areas on the film.
Supporting Figure 5.4.3 – Average water contact angle of DMP copolymers blade coated on glass. Error bars represent the standard deviation of three measurements.

Supporting Figure 5.4.4 – Absorption spectra of pristine BOE-DMP film (black), dry OH-DMP film after hydrolysis/rinsing (red), and OH-DMP film after electrochemical conditioning while holding at -0.4 V vs. Ag/AgCl in 0.1 M NaCl/H$_2$O (blue).
Supporting Figure 5.4.5 – Potential-dependent $C^*$ of blade-coated films of BOE-DMP and OH-DMP in degassed 0.1 NaCl/H$_2$O. $C^*$ was extracted from EIS and normalized to the volume of the dry de-doped film. Error bars for OH-DMP represent the standard deviation of 3+ films, cast and measured separately.
Supporting Figure 5.4.6 – Differential pulse voltammograms of thin films of polar PPProDOTs: A) G2-DMP, B) G3-DMP, C) G4-DMP, D) OH-DMP and E) BOE-DMP, labeling the oxidation onsets. Polymer films were drop-cast on a GC button electrode and studied in a degassed 0.1 M NaCl/H₂O electrolyte under an argon blanket. Solid lines indicate data. Dashed lines indicate tangents for onset extraction.
Supporting Figure 5.4.7 – Scan rate dependence of CV peak current density for the aqueous-compatible polar ProDOT polymers: A) G2-DMP, B) G3-DMP, C) G4-DMP, and D) OH-DMP. Points connected with solid lines represent experimental peak current density. Dashed line represents the linear projection of peak current density, as determined by data recorded within non-diffusion limited scan rate regimes ($v \leq 50$ mV s$^{-1}$) and fit to a linear regression.
Supporting Figure 5.4.8 – Comparison of G3-DMP (shown here as “ProDOT(G3)-DMP”) and p(g3T2-T) from CHAPTER 4, showing A) percent charge retention over 1,000 doping/de-doping cycles in 0.1 M NaCl/H$_2$O for drop-cast p(g3T2-T) and 0.5 M NaCl for spray-cast G3-DMP. Identical voltage windows were used in the long-term cycling. B) CV traces of films (16 μg total mass) drop-cast on GC button electrode.
Supporting Figure 5.4.9 – Potential-dependent absorption spectra of A) polymer BOE-DMP and B) polymer OH-DMP blade-coated on ITO/glass and biased in 0.1 M NaCl/H₂O.
Supporting Figure 5.4.10 – Absorption spectra of blade- and spray-coated films of de-doped G3-DMP (“G3”) on ITO/glass while biased in 0.1 M NaCl/H₂O. Spectra are recorded after electrochemical conditioning under potentiostatic conditions. Potentials are reported vs. Ag/AgCl.
Supporting Figure 5.4.11 – Normalized UV-Vis absorption spectra of films cast onto ITO/glass, including pristine/as-cast BOE-DMP, conditioned/de-doped BOE-DMP in an organic electrolyte (-0.8 V vs. Ag/Ag⁺ in 0.5 M TBAPF₆), and condition/de-doped OH-DMP in an aqueous electrolyte (-0.8 V vs. Ag/AgCl in 0.1 M NaCl/H₂O).
Supporting Figure 5.4.12 – UV-Vis-NIR absorption spectra of films of two different batches of G3-DMP held at -0.8 V vs. Ag/AgCl in 0.1 M NaCl. The batches, which were synthesized by different individuals, were found to have a different GPC-determined molecular weights (in CHCl3 at 40 °C vs. PS). Purple line: G3-DMP-JFP-22k, $M_n = 22$ kDa, $D = 2.0$. Red line: G3-DMP-BTD-41k, $M_n = 41$ kDa, $D = 2.5$. 
Supporting Figure 5.4.13 – Potential-dependent in situ conductance (black circles) and linear optical absorbance (red squares) at 1.31 eV (935 nm), corresponding to the polaron state, for spray-cast films of G3-DMP. Measurements were performed on electrochemically doped films in ambient 0.5 M NaCl/H₂O.

Supporting Figure 5.4.14 – Two-dimensional representative GIWAXS pattern for G3-DMP films cast by A) blade-coating from chloroform and B) spray-coating from chloroform. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale.
Supporting Figure 5.4.15 – Two-dimensional representative GIWAXS pattern for G2-DMP films cast by A) spray-coating and B) spin-coating from chloroform. Scattering intensities are normalized to film thickness and represented linearly, following a purple-red color scale.

Supporting Figure 5.4.16 – Two-dimensional representative GIWAXS patterns of A) pristine blade-coated BOE-DMP, and B) OH-DMP, accessed through hydrolysis of blade-coated BOE-DMP. Scattering intensities represented linearly, following a purple-red color scale. Note that absolute scattering intensities cannot be compared, as the data were collected at different beamlines. Red line in panel B is an artifact of the detected and ought to be ignored.
Supporting Figure 5.4.17 – Representative iOECT characteristics for devices fabricated with G2-DMP, showing A) Transfer characteristics and corresponding transconductance, \(V_D = -0.60\) V, B) Transfer curve on logarithmic scale superimposed on drain current. C) Output curves. Arrows indicate direction of the sweep.
Supporting Figure 5.4.18 – Representative iOECT characteristics for devices fabricated with G3-DMP, showing A) Transfer characteristics and corresponding transconductance, $V_D = -0.60$ V, B) Transfer curve on logarithmic scale superimposed on drain current. C) Output curves. Arrows indicate direction of the sweep.
Supporting Figure 5.4.19 – Representative iOECT characteristics for devices fabricated with G4-DMP, showing A) Transfer characteristics and corresponding transconductance, $V_D = -0.60$ V, B) Transfer curve on logarithmic scale superimposed on drain current. C) Output curves. Arrows indicate direction of the sweep.
Supporting Figure 5.4.20 – Potential-dependent in situ conductance (black squares/lines) and transfer curve from a four-electrode OECT-like measurement (purple line, $V_D = 0.4$ V, $\nu = 50$ mV s$^{-1}$) for G3-DMP films coated on interdigitated electrodes and studied under ambient conditions in a NaCl/H$_2$O electrolyte solution.
5.5 Additional Experimental Details

Potential-dependent in situ conductance measurements were performed on film of G3-DMP spray-cast from chloroform on gold interdigitated electrodes (MicruX, 10 μm gap, 10 μm finger width, 15 pairs of fingers). Films were configured into a four-electrode (two WE) cell using an Ag/AgCl reference (3 M NaCl, BASi), a platinum flag counter electrode, and a 0.1 M aqueous NaCl electrolyte in ultrapure water using the MicruX AIO Batch Platform. Data was recorded using a Pine AFCBP 1 bipotentiostat with Aftermath software (DEVC program in collection mode). To measure the apparent conductance of the assembly, both WEs were biased at a DC offset (0.7 to +0.7 V vs. Ag/AgCl). To one of the WEs, an additional 5 mV AC waveform was superimposed on the DC offset. The slopes of the linear I-V traces were used to determine the apparent conductance, as described more thoroughly in the literature.\textsuperscript{129,209} For collecting the OECT-like transfer curve in this four-electrode configuration, the cell was configured in an identical way but was biased in DEVC window mode with a WE2 offset voltage of 0.4 V and a WE1 scan rate of 50 mV s\textsuperscript{-1}.

More information about the fabrication testing of pOECT devices as well as EIS measurements performed on G3-DMP at NU can be found in the cited literature.\textsuperscript{227}

Details concerning electrochemical characterization, UV-Vis-NIR absorption spectroscopy, EIS (performed at GT), GIWAXS, substrate/electrode preparation, iOECT device measurements, and AFM (performed on Si substrates) can be found in CHAPTER 2. Polymer synthetic procedures and chemical characterization that are not available in the literature are reported in the APPENDIX.
Films were processed by casting from chloroform solution. Details can be found in CHAPTER 2.2. For spray-coating, G2-DMP was dissolved at 4 mg mL⁻¹ in chloroform and spray-cast onto room-temperature substrates. For blade-coating, polymers were dissolved at 15 mg mL⁻¹ in room temperature chloroform by stirring in a closed vial overnight. The solutions were blade-coated using a custom-built blade coater consisting of a clean and unmodified glass blade. The gap height was 150 μm and the blade was pulled at a speed of 4 mm s⁻¹. The blade-coating stage was heated to 30 °C while coating. Films of thicknesses ranging from 100–250 nm were obtained. Drop-cast films were used for CV and DPV. For drop-casting, polymers were dissolved in room-temperature chloroform overnight at a concentration of 4 mg mL⁻¹. Identical masses of each polymers were drop-casted (four 1-μL aliquots, 4 μL total volume, 16 μg total polymer mass) onto a polished glassy carbon button electrode (active area = 0.07 cm²).

To access OH-DMP, the polymer BOE-DMP was cast from solution onto the electrode substrate via blade-coating or drop-casting. The substrate was then suspended with tweezers into a solution of 2 M KOH in methanol heated to 55 °C for 4 hours while the solution gently stirred. During the side chain saponification process, white solid particulates accumulated in the KOH solution and on the surface of the film. After the hydrolysis was complete, the film was gently rinsed with clean methanol or water/methanol and allowed to dry at room temperature.

Aqueous CV and DPV performed on a Reference 3000 Gamry potentiostat/galvanostat/ZRA controlled with Gamry Framework 6.5 software. CV was performed from -0.8 to +0.8 V vs. Ag/AgCl at scan rates ranging from 2–2000 mV s⁻¹. Scan rate dependence of BOE-DMP was not performed due to its poor redox activity and
stability in aqueous NaCl. All aqueous electrochemical characterization was performed in a degassed solution of 0.1 M NaCl (biotechnology grade, Amresco) in ultrapure water (18.2 MΩ·cm) while under an argon blanket. A glassy carbon rod was used as the counter electrode, and an Ag/AgCl electrode (3 M NaCl/H2O inner solution, BASi) was used as the reference.

Electrochemical impedance spectroscopy (EIS) was performed on a Reference 3000 Gamry potentiostat/galvanostat/ZRA utilizing the Gamry Framework 6.5 software. Films for Polymers G3-DMP, G4-DMP, BOE-DMP, and OH-DMP were obtained by blade-coating from precursor solutions on clean ITO/glass slides as described above. G2-DMP was spray-cast from a dilute solution as described above. The irregular portions of the film were removed by wiping with a cotton swap, yielding rectangular films. The polymer-coated ITO electrode was configured as a working electrode into a three-electrode cell. A large stainless-steel plate was used as the counter electrode, and Ag/AgCl electrode (3 M NaCl/H2O inner solution, BASi) was used as the reference. The cell was filled with a 0.1 M NaCl aqueous electrolyte (in ultrapure water) degassed with argon. The cell was and kept under an argon blanket throughout the entirety of the EIS studies. The working and counter electrodes were positioned 1 cm apart, with the polymer-coated side of the ITO electrode directly facing the stainless-steel plate.

Prior to performing EIS studies, the films were electrochemically conditioned via 10 cyclic voltammograms from -0.8 to +0.8 V vs. Ag/AgCl at 50 mV/s. For potential-dependent EIS, a 5 mV AC bias was superimposed on a range of DC biases, which set the oxidation state/doping level of the polymer. Film were held at a given potential for 60 seconds before the EIS measurement gun ensure steady-state behavior. The measurement
was performed starting with the film in its most de-doped state and increasing anodically to its most p-doped state. EIS was performed at low frequencies (10 Hz–0.1 Hz) to capture the capacitance associated with the faradaic doping/de-doping reaction. The experimental impedance spectra were fitted using the Zview software as explained in more detail in CHAPTER 2.3.4.

Once the EIS measurement was complete, the films were de-doped by holding at -0.8 V vs. Ag/AgCl for 30 s. Next, the films were rinsed with copious amounts of DI water and dried at room temperature. To calculate the volume of the film, the thicknesses of the dry films were measured using a Bruker Dektak XT profilometer, while the film length and width were calculated using manual calipers. The calculated capacitance C was normalized to film volume to give the volumetric capacitance $C^*$. At least three separate films of comparable film thicknesses (100–250 nm) were studied for each polymer to ensure reproducibility of the impedance characteristics and $C^*$ value.

FT-IR was recorded on a Shimadzu Prestige Infrared Spectrometer using solid polymer samples. BOE-DMP was blade coated onto an ITO/glass substrate and hydrolyzed to OH-DMP, as described previously. The product OH-DMP polymer was rinsed, scraped from the electrode, and dried under vacuum prior overnight prior to FT-IR analysis.
CHAPTER 6. STRUCTURE-DEPENDENT VOLUMETRIC AND INTERFACIAL BEHAVIOR IN THE ELECTROCHEMICAL DOPING OF AQUEOUS-COMPATIBLE POLY(PRODOTS)

This chapter includes unpublished content adapted from a working manuscript that is currently in preparation, as tentatively referenced below:


6.1 Introduction

6.1.1 Complexities of Electrochemical Doping

The controlled coupling of ionic and electronic charges in π-conjugated polymers underpins a range of exploratory electrochemical devices, with applications ranging from charge storage to biomaterials (see CHAPTER 1). In these applications, the electrochemical doping of the polymer active layer is a critical component of device functionality. The doping reaction is a complex and dynamic process characterized by substantial ion and solvent fluxes across the polymer-electrolyte interface, which is accompanied by structural reorganization of the polymer active layer. Along with the transport of ions and solvent, electronic charge carriers (electrons/holes) must be transported through the depth of the polymer film and transferred across the polymer-
electrode interface. This faradic charge transfer, which is required to effectuate the doping reaction, is associated with substantial changes in carrier mobility and ion content in the bulk of the film. In this vein, these redox-active conjugated polymers are commonly referred to as polymeric or organic mixed ionic-electronic conductors (OMIECs or PMIECs), that is, they exhibit the relatively uncommon property of simultaneous ionic and electronic transport.

Notably, these two types of transport are intimately coupled in π-conjugated polymers by an electroneutrality condition: To introduce mobile charge carriers, counter ions must penetrate the polymer film and stabilize polaronic and bipolaronic states formed along the π-conjugated backbone. Yet, enhancing both ionic and electronic transport generally requires two competing materials design criteria. Effective ionic conduction usually necessitates amorphous polymer structures with high free volume to promote swelling and ion transport. Meanwhile, delocalization and transport of electronic charge carriers usually require higher degrees of order and crystallinity. Thus, electrochemical doping processes can be difficult to engineer and optimize for a given application.

6.1.2 Volumetric and Interfacial Fluctuations

The mass transport processes required for doping are frequently associated with physical expansion and contraction of the active layer. Such chemomechanical processes are highly sensitive to polymer structure, film morphology, electrolyte composition, osmotic forces, as well as unique polymer-polymer or polymer-electrolyte interactions in the film.
For some applications, like artificial muscles, structural deformation is necessary to mimic the controlled bending and stretching of native biological tissues.\textsuperscript{11} For other devices, like electrochromic displays, repeated mechanical deformations of the active layer is thought to result in instabilities in polymer-electrode adhesion, leading to device failure.\textsuperscript{293,464} In the field of organic electrochemical transistors (OECTs), hydration of the active layer has been shown to drastically influence charge carrier transport and the overall electrochemical stability of the system.\textsuperscript{223,370,416} When comparing OECT active materials with drastically different redox activity, greater swelling is usually observed in the polymer with the stronger electrochemical response. This has led to the incomplete hypothesis that greater swelling is associated with enhanced OECT performance.\textsuperscript{194,231,465} However, when comparing active materials with similar redox activity in the device electrolyte, the relationship between volumetric swelling and performance is less straightforward. For ethylene glycol-functionalized polythiophenes, it has been shown that swelling is not de facto beneficial for device operation and may actually disrupt charge carrier transport, especially if swelling occurs heterogeneously within the film.\textsuperscript{370,373} In fact, some of the highest performing OECT active materials exhibit little swelling at all upon electrochemical doping. For instance, OECTs with channels comprised of highly crystalline PEDOT:PSS exhibited record-breaking device performance and stability without undergoing significant volumetric changes upon doping/de-doping.\textsuperscript{223}

Considering these observations, it is not only important to understand the role of swelling in device performance, but it is also necessary to establish the fundamental relationships between swelling, polymer structure, and redox properties. This level of insight is crucial for the rational design of OMIECs targeted for different applications.
Moreover, the characteristics that govern passive swelling (i.e., swelling upon exposure to an electrolyte with no bias applied) and active swelling (i.e., the potential-dependent swelling that occurs upon doping) are not clearly delineated. Passive swelling may predominantly be dictated by film microstructure, available free volume, polymer-electrolyte compatibility, and entropic effects associated with mixing and conformational freedom. Active swelling, on the other hand, may depend on additional factors, such as doping density, ion-solvent partition, chain rearrangement upon doping, and coulombic interactions.

In addition to these volumetric changes, there are also interfacial fluctuations that occur with electrochemical doping. A recent study by Matta et al. proposed that the nature of the electrolyte ion influences both the magnitude of passive swelling and the extent of ion accumulation at the polymer-electrolyte interface.\textsuperscript{461} Additional capacitive charging effects of internal interfaces may also occur upon doping, giving rise to compositional and potential gradients within the film. Partial solvation of the OMIEC layer also increase the diffuseness of the polymer-electrolyte interface, which in turn may impact the homogeneity of carrier density of transport.

Despite the importance of these volumetric and interfacial effects, the structural factors that influence such physical changes are not well understood. Moreover, it is not clear to what extent (if at all) physical properties like swelling influence electrochemical properties and vice versa.

When studying doping processes in OMIECs, traditional electroanalytical methods are useful for understanding redox reactions and establishing general relationships across
a series of materials. However, such techniques fall short when seeking to develop a complete picture of the volumetric and interfacial properties coupled to the doping reaction. While it can be difficult to monitor to these physical processes in situ, such approaches are necessary to accurately describe all aspects of material behavior. Thus far, several different techniques have been used to directly study the physical changes that occur upon electrochemical doping. These methods include scanning probe techniques,\textsuperscript{293,370,373,460,464,466} optical microscopy,\textsuperscript{294} EQCM-D,\textsuperscript{292,416,467,468} strain gauge measurements,\textsuperscript{459} and more recently, in situ X-ray scattering.\textsuperscript{414}

6.1.3 Potential Utility of Neutron Reflectivity

One technique that is less widely used to study actuation and ion uptake in OMIECs is neutron reflectivity (NR). This technique offers several unique advantages for studying swelling in conjugated polymer films. Unlike X-ray scattering, which depends on electron density and therefore the atomic number, neutron scattering depends on the properties of the constituent nuclei in a sample. Therefore, neutron methods are advantageous for studying carbon-based materials, like polymers, which otherwise would be difficult to study with X-rays, especially in the presence of heavier elements. Because neutrons are sensitive to different isotopes, the contrast of a sample can be tuned by isotopic substitution. This allows for specific components of a system or process to be selectively studied.

Neutrons also have a greater penetration ability than X-rays. Accordingly, neutrons can be used to characterize so-called “buried interfaces,” i.e. interfaces that lie within multi-layered systems. Neutron reflectometry has been extensively used to characterize
interfacial processes in electrochemical systems that are “buried” beneath layers of electrolyte. For instance, NR has been performed to track ion intercalation, double layer formation, and solid-electrolyte interphase formation in situ while electrochemically cycling.\textsuperscript{334,469–473}

The ability of neutrons to “see” into polymer films also gives NR an advantage over methods like EQCM-D. Both techniques can detect bulk changes in a film’s thickness and density upon swelling, but only NR can be used to also study interfacial or depth-dependent changes occurring within the film. Provided sufficient nuclear contrast, NR also allows for extraction of absolute solvation and composition, while EQCM-D only allows one to monitor changes in these properties.

When compared to scanning probe techniques, which provide powerful local descriptions of processes at the nano- and micro-scale, neutron reflectometry offers surface-averaged measurements over the area of the entire beam footprint (~cm in diameter). Thus, data from NR is thought to provide a more holistic and statistically representative picture of the changes occurring in the sample. (For details regarding NR more generally as a technique, the reader is directed to CHAPTER 2.7 and the references therein.)

In the field of redox-active polymers, there are a few examples showcasing how NR can be used to study swelling and interfacial processes in situ. Most published studies involved non-conjugated redox polymers containing redox-active metal centers, such as iron or osmium.\textsuperscript{474–476} Neutron reflectometry has also been applied to redox-active \(\pi\)-conjugated polymers, albeit to a lesser extent. Many of these studies surround the
electropolymerized PPy. Hillman et al.\textsuperscript{477} used NR to study the morphology of electropolymerized CP composites. In work reported by Beebee et al., NR was employed to evaluate the effect of electropolymerization conditions on the density, thickness, solvent content of PPy films.\textsuperscript{478} In the early 1990s, several NR studies were performed on electropolymerized poly(bithiophene) films at different doping levels.\textsuperscript{333} This work found that the outer-most layer of the film is diffuse and enriched with solvent, while the inner-most portion of the film at the electrode interface is generally dense, compact, and unsolvated. Changes in thickness and interfacial diffuseness were observed upon p-doping. In sum, while NR holds immense promise for elucidating physical changes associated with electrochemical doping, its potential remains unrealized. The few studies that have been done were limited to electropolymerized materials, which are currently less favored than soluble polymers synthesized by non-electrochemical means. Given the relatively small range of materials tested, the existing body of work also did not establish any comprehensive structure-property relationships regarding the swelling characteristics and interfacial properties of doped materials. For instance, NR has not been applied to any OMIECs functionalized with ethylene glycol (EG)-based side chains, which are of particular interest to the field considering their aqueous redox activity and potential use in bioelectronic devices.

6.1.4 Goals of Study

With these considerations in mind, \textit{in situ} neutron reflectivity may provide unique insights into the potential-dependent physical properties of solution-processable, aqueous-compatible OMIECs. Accordingly, this work utilizes NR as a method for directly probing
the swelling and electrolyte uptake in two polar-functionalized poly(3,4-propylenedioxythiophenes) (PProDOTs) while electrochemically doping in aqueous media. Specifically, this chapter seeks to answer the following questions about the polymers:

(i) Do the polar PProDOTs swell passively upon exposure to an aqueous electrolyte, even without application of a bias?

(ii) What are the structural and compositional changes induced by electrochemical conditioning (i.e. the “break-in” effect)?

(iii) To what extent do these materials swell upon doping, and how does the swelling evolve with doping level?

(iv) What is the structure and composition of the polymer-electrode and polymer-electrolyte interface? Does this differ from the bulk?

(v) How does the polymer side chain structure influence these properties?

The active materials of interest include two ProDOT-based alternating copolymers: G3-DEHP and G3-DMP (Figure 6.1.1). As explained in previous chapters, PProDOT-based materials are ideal for electrochemical applications due to their versatile structure, electron richness, solution processability, and stability. Both polymers consist of two ProDOT-based comonomers. One comonomer (G3) is functionalized with highly polar EG-based side chains, and the second comonomer (DMP or DEHP) is functionalized with non-polar substituent groups.

The polar EG side chains impart greater solubility and hydrophilicity to the material, thereby conferring aqueous redox activity. Aqueous redox activity is particularly
important when establishing structure-property relationships that can be applied to materials used in bioelectronic devices, such as OECTs, where the ability of the OMIEC to support hydrated ion transport is essential. Moreover, the use of an aqueous electrolyte allows for the NR contrast to be readily modified. The contrast in neutron scattering originates from variations in the scattering length density (SLD) of the components in the sample. As explained in CHAPTER 2.7, a material’s SLD is a function of its constituent nuclei and therefore is isotope-sensitive. When using an aqueous electrolyte, the SLD of the solvent can be easily tuned by incorporation of D₂O. Such “contrast-matching” strategies allow for certain phenomena to be isolated and probed separately.

Figure 6.1.1 – Repeat unit structures of two polar-functionalized PProDOT copolymers, G3-DEHP and G3-DMP, which differ in the substitution of the aliphatic comonomer.
While both polymers incorporate the G3 ProDOT unit, they differ in the functionalization of the second comonomer. Polymer G3-DMP, which was studied in CHAPTER 5 and has been reported elsewhere,\(^{227,417}\) includes a 2,2-dimethyl-ProDOT (DMP) comonomer with methyl substituents on the 2-position of the propylenedioxy bridge. Based on findings presented on polythiophenes in CHAPTER 4, this minimally functionalized unit is hypothesized to promote ordering by facilitating inter-chain interactions. In G3-DEHP, the 2-position of the ProDOT unit is functionalized with branched aliphatic ether (ethylhexyloxy) groups. Consequently, G3-DEHP has an overall lower electroactive mass and greater hydrophobic character than G3-DMP. Owing to the long, sterically bulky ethylhexyloxy side chains, G3-DEHP may also experience greater steric interactions, resulting in weaker inter-chain coupling and perhaps greater free volume.

By combining electrochemical methods and in situ neutron reflectivity, the doping process of G3-DMP and G3-DEHP will be compared, both with respect to the underlying redox reaction and the concurrent physical changes occurring in the film. Such studies will provide unique insights into the impact that side chain density and hydrophilicity have on the behavior of the OMIEC. In this work, we aim to better understand the relationship between polymer structure and the myriad of complex physical changes occurring with the doping reaction. Furthermore, we seek to demonstrate the utility of neutron reflectivity as a versatile in situ technique for monitoring volumetric and interfacial processes in OMEICs.
6.2 Results and Discussion

6.2.1 Polymer Design and Preparation

Polymers G3-DEHP and G3-DMP were prepared by Pd-catalyzed direct hetero(arylation) polymerization (DHAP) by Brandon Ditullio (GT) and Dr. James Ponder (ICL/GT), respectively. The synthetic procedures and chemical characterization ($^1$H-NMR, $^{13}$C-NMR, elemental analysis, GPC, etc.) for G3-DEHP and its precursors are reported in the APPENDIX. Polymer G3-DMP was synthesized and characterized following literature procedures.227

Based on GPC measurements performed against a PS standard (CHCl$_3$, 40 °C), the estimated molecular weights and dispersities were found to be similar for G3-DEHP ($M_n = 24$ kDa, $\bar{D} = 1.5$) and G3-DMP ($M_n = 26$ kDa, $\bar{D} = 1.9$). Variables influencing the apparent GPC-determined molecular weight are discussed briefly in CHAPTER 4.2.1 and CHAPTER 5.2.1.2 and therefore will not be reiterated here. Because the extent of swelling can be influenced by changes in free volume (e.g. chain ends), it is important to ensure that the approximate molecular weights and dispersity of the two polymers are comparable.

6.2.2 Doping in Aqueous Media

6.2.2.1 Electrochemical Properties

To understand how the side chain structure influences the aqueous redox properties of the PProDOTs, the polymer films were characterized by differential pulse voltammetry (DPV, Supporting Figure 6.4.1), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). Seeing as many of the projected applications of OMIECs involve
bioelectronic devices (electrophysiological probes, biosensors, ion pumps, etc.), the electrolyte salt was chosen to be NaCl to mimic the ionic environment of biological systems.

As with many π-conjugated polymers, the first CV sweeps of the pristine PProDOTs films are slightly different than subsequent scans. This so-called “electrochemical conditioning” or “break-in” effect, which was discussed in CHAPTER 2.3 (pp. 60), is thought to arise from a reorganization of polymer chains to facilitate electrolyte uptake and stabilize charge carriers. For both G3-DEHP and G3-DMP, anywhere from 3–10 full doping/de-doping CV scans are required to yield consistent, overlapping CV characteristics. The extent of the break-in and the number of scans required to condition the films depends on a number of factors, such as film thickness, processing method, polymer structure, extent of aggregation in solution, biasing conditions, etc. Comparing the first and tenth CV scans of G3-DEHP and G3-DMP shows that the break-in process results in an overall lowering of the oxidation onset (E_{ox}) of both polymers (Supporting Figure 6.4.2). For other PProDOTs, the lowering of E_{ox} upon break-in is hypothesized to represent the formation film domains with increased “electrochemical accessibility,” i.e. longer effective conjugation lengths and/or enhanced aggregation.129

Following electrochemical conditioning, the characteristics of the film correspond to a more representative and reproducible state and therefore can be analyzed more thoroughly. When comparing the current response of G3-DEHP and G3-DMP, it is evident that incorporation of the large, hydrophobic side chains in G3-DEHP has a drastic effect on the redox properties. The E_{ox} of G3-DEHP (+0.28 V) is nearly 0.5 V greater than that of G3-DMP (-0.25 V), as shown in Table 6.2.1. Note that the E_{ox} #1 of this batch of G3-
DMP, which was studied in 0.5 M NaCl, is very similar to the \( E_{\text{ox}} \) #1 for the other batch of G3-DMP presented in CHAPTER 5, which was studied in 0.1 M NaCl (\( E_{\text{ox}} \) #1 = -0.22 V, Table 5.2.1, Supporting Figure 5.4.6).

### Table 6.2.1 – Redox properties of G3-DEHP and D3-DMP films in a 0.5 M NaCl/H\(_2\)O electrolyte. Potentials are reported vs. Ag/AgCl.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( E_{\text{ox}} ) (#1) (V)(^a)</th>
<th>( E_{\text{ox}} ) (#2) (V)(^a)</th>
<th>( C^* ) (F cm(^{-3}))(^b)</th>
<th>( E_C ) (V)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3-DEHP</td>
<td>+0.28</td>
<td>-</td>
<td>90</td>
<td>+0.70</td>
</tr>
<tr>
<td>G3-DMP</td>
<td>-0.25</td>
<td>+0.21</td>
<td>81</td>
<td>+0.40</td>
</tr>
</tbody>
</table>

\(^a\) Determined by DPV.
\(^b\) Determined by EIS.

The CV trace of G3-DMP in 0.5 M NaCl/H\(_2\)O is quite broad, showing multiple oxidation processes over a wider electrochemical window (Figure 6.2.1). This behavior is identical to the behavior observed for G3-DMP studied in 0.1 M NaCl/H\(_2\)O, as presented in CHAPTER 5 (Figure 5.2.3B). As described previously, the different oxidation waves are thought to arise from the sequential doping of film domains with different extents of order or aggregation.\(^{255,257,380}\) Meanwhile, the CV of G3-DEHP in 0.5 M NaCl only shows one prominent oxidation process and reaches a maximum current close to the electrochemical window of water.

One possible explanation for the enhanced electroactivity of G3-DMP lies in the relative hydrophobic-hydrophilic balance of each material. The longer alkyl side chains
appended to G3-DEHP may obstruct aqueous electrolyte uptake, resulting in a polymer that is more difficult to oxidize and less electroactive in water. To test this possibility, the polymers were also electrochemically cycled in an organic electrolyte (TBAPF$_6$ in propylene carbonate). In this environment, the hydrophobicity of a polymer is expected to play less of a role in its redox response. Even in the organic electrolyte, G3-DMP still has a lower $E_{ox}$ and is more electroactive than G3-DEHP (Supporting Figure 6.4.3). This result suggests that the redox behavior of the two polymers is, in fact, fundamentally different, and that the aqueous CVs cannot be explained by differences in hydrophilicity alone.

Instead, it seems as though the low $E_{ox}$ and enhanced electroactivity of G3-DMP is due to incorporation of the minimally substituted DMP unit, which lowers the overall side chain density of the polymer. As shown for EG-functionalized PTs in CHAPTER 4, incorporation of a minimally substituted “spacer” unit into the backbone facilitates intermolecular organization of the π system, thereby lowering IE and $E_{ox}$. Functionalization of every aromatic unit with a bulky or long side chain, on the other hand, prevents intermolecular ordering and raises IE and $E_{ox}$. Here, we see a similar relationship with these PProDOTs, where the addition of the sizable ethylhexyloxy side chains in G3-DEHP results in a greater $E_{ox}$. In other words, it is not the hydrophobicity of the side chains on the DEHP unit that determine the redox response in water; rather, it is the presence of any side chain density on the comonomer at all. Considering that the branched ethylhexyloxy side chains are placed rather far away from the backbone, we posit that this effect is chiefly inter-molecular in origin, rather than an intra-molecular effect associated with backbone twisting. This hypothesis will be revisited later in this chapter.
To further evaluate the redox behavior of G3-DEHP and G3-DMP, the peak current density of the CV was monitored for CVs recorded at different scan rates (Figure 6.2.1B). For G3-DMP, the relationship between the peak current density and scan rate roughly follows a linear projection up to 2,000 mV s$^{-1}$. This is indicative of oxidation/reduction of...
an adsorbed species limited by kinetics and not diffusion. Such behavior is similar to the scan rate dependence shown for the same material in 0.1 M NaCl (Supporting Figure 5.4.6), with slight differences arising from variations in electrolyte concentration and conductivity.

On the other hand, electrochemical doping of G3-DEHP is much more diffusion-limited than the doping of G3-DMP. The peak current density for G3-DEHP only follows a linear projection up to ~750 mV s⁻¹ (Figure 6.2.1B). At higher scan rates, the relationship deviates from a linear trend and assumes a square-root dependence, which is a characteristic of a diffusion-limited process (for more information, see CHAPTER 2.3.1 and references therein). Presumably, this diffusion limitation arises from counter ion transport through the depth of the film. Despite the longer branched side chains in G3-DEHP (which one may expect to increase the free volume of the film and enhance ion transport), ion diffusion appears to be more limited in this material.

In addition to the voltammetric techniques described below, both polymers were studied by EIS over a range of DC offsets. The low-frequency EIS data was fit as described previously (CHAPTER 2.3.4) to extract the steady-state volumetric capacitance (C*) of both materials. Based on widespread models, C* is thought to be a predictor of performance in OECTs, as it describes the density of charge carriers injected into the OMIEC over a finite operating potential.²⁰¹ Consistent with the results from cyclic voltammetry, G3-DMP shows capacitive behavior over a wider potential window than G3-DEHP (Supporting Figure 6.4.4). As determined by EIS, the peak C* of G3-DEHP (~90 F cm⁻³) is slightly higher than that of G3-DEHP (~80 F cm⁻³). So while G3-DMP has a more capacitive dynamic response over a wider voltage range, polymer G3-DEHP shows a
higher steady-state C* when measured at a single potential, as more of the doping reaction occurs within a narrow potential window.

6.2.2.2 Optical Properties

To gain additional insight into the behavior of G3-DEHP and G3-DMP in aqueous media, the UV-Vis-NIR absorption spectra of the polymers were recorded in different environments. For pristine films in their as-cast state, the π-π* absorption bands show some weak vibronic coupling. Both G3-DMP and G3-DEHP are partially doped in their pristine state, as evidenced by the absorption in the NIR (Supporting Figure 5.4.12).

As described for the previous measurements, the films were electrochemically conditioned by performing ten CV scans. After this “break-in,” the absorption spectra of the de-doped films were recorded. As shown in Supporting Figure 6.4.5A, the “break-in” of G3-DEHP is characterized by an overall increase in intensity of the π-π* transition, as the polarons in the as-cast film are converted to neutral species. However, the optical gap (E_{opt}, as determined by the high-energy absorption onset) and absorption line shape do not change significantly. The break-in of G3-DMP involves more notable changes; the E_{opt} is lower and the fine structure of the π-π* transition appears different (Supporting Figure 6.4.5B).

When comparing the absorption spectra of both G3-DEHP and G3-DMP in their de-doped states, several differences can be observed (Figure 6.2.2). First, the E_{opt} of G3-DMP (673 nm, 1.84 eV) is slightly red-shifted relative to the E_{opt} of G3-DEHP (626 nm, 1.98 eV), suggesting a smaller HOMO-LUMO gap. For this particular pair of PPProDOTs, the narrowing of the HOMO-LUMO gap can be explained by either (i) an increase in
richness, perhaps due to geometric changes in the propylenedioxy bridge, and/or (ii) the presence of interactions giving rise to longer effective conjugation lengths.

The absorption line shape also differs for the two polymers, with G3-DMP showing a relatively suppressed 0-0 vibronic transition ($A_{0-0}$) relative to the 0-1 transition ($A_{0-1}$). This was also noted in Figure 5.2.6 for a de-doped G3-DMP film immersed in a more dilute electrolyte solution. While it is unclear how rigorously and quantitatively the absorption line shape of these PProDOTs can be examined (see related discussion in CHAPTER 5.2.3), the overall line shape of G3-DMP resembles that of rr-P3H. Depending on the environment and processing method, rr-P3HT usually also shows $A_{0-0}/A_{0-1} < 1$. In the context of the hybrid HJ aggregate model, $^{387,393}$ which is commonly used to quantitatively analyze the absorption line shape of P3HT, a $A_{0-0}/A_{0-1}$ ratio less than unity is characteristic of a photophysical aggregate favoring H-type (inter-chain, through-space) coupling. Assuming the G3-DMP behaves as a photophysical aggregate (in which the transition dipole moments of neighboring and adjacent chromophores are interacting), its absorption line shape would be indicative of enhanced inter-chain coupling.

In contrast to G3-DMP, the absorption line shape of G3-DEHP has approximately equal intensities of $A_{0-0}$ and $A_{0-1}$. The relative enhancement of the $A_{0-0}$ transition is characteristic of more J-type aggregation arising from either increased intra-chain coupling or decreased inter-chain coupling. The absorption profile of G3-DEHP is less like that of rr-P3HT and more closely resembles the ordered phases of MEH-PPV$^{479}$ and polyfluorene, $^{480}$ which also show an enhanced $A_{0-0}$ intensities. MEH-PPV aggregates are thought to behave like a collection of J-aggregates with properties resembling that of single
chains. Considering these observations, we hypothesize that G3-DEHP exhibits more J-aggregation than does G3-DMP.

Intuitively, one can imagine how the large and sterically bulky ethylhexyloxy side chains in G3-DEHP would obstruct effective stacking of neighboring \( \pi \)-conjugated chain segments, thereby reducing the extent of inter-chain coupling and resulting in greater J-aggregate character. Meanwhile, the minimally substituted DMP unit, which is functionalized with only small methyl groups, may allow for greater interaction between chain and promote H-aggregation. The enhanced inter-molecular coupling in G3-DMP may explain its lower \( E_{\text{ox}} \) and greater electroactivity.

As explained earlier in CHAPTER 5.2.3, the fundamental photophysical behavior of PProDOTs is not as widely studied as it is for other polymers like P3HT and MEH-PPV. Accordingly, there is not a strong understanding regarding the factors that determine the absorption line shape and how the line shape can be related to chromophore arrangement. Accordingly, strong conclusions cannot be drawn from the UV-Vis absorption spectra of G3-DMP and G3-DEHP. Instead, the hypotheses presented here are highly speculative, and we note only qualitative differences that suggest differences in the nature of the polymer arrangement in the neutral and doped states. Additional spectroscopic studies, both for films and solutions, would be incredibly valuable for developing a description of the photophysical properties of new and existing PProDOTs.
Figure 6.2.2 – Normalized UV-Vis absorption spectra of neutral PProDOTs films after electrochemical conditioning. Spectra were recorded while applying de-doping potentials (0.0 V for G3-DEHP and -0.4 V for G3-DMP) in 0.5 M NaCl/H₂O.

To further characterize the electrochemical doping of G3-DEHP and G3-DMP in aqueous media, the UV-Vis-NIR absorption spectra of both films were recorded as a function of electrochemical potential (Figure 6.2.3). With increasing potential, both polymers undergo a bleaching of the $\pi-\pi^*$ transition accompanied by growth of absorbance of polaronic and bipolaronic species around 900 nm and further into the NIR. At the highest potential tested (+0.8 V vs. Ag/AgCl), G3-DMP shows virtually no absorption from neutral species or polarons. Only the absorption tail of the bipolaron band is apparent at this doping level. At the same potential, G3-DEHP shows minimal absorption from neutral species.
(~475 nm), but it largely converted to its charged state. This indicates that both polymers can be effectively p-doped in aqueous media.

Figure 6.2.3 – Potential-dependent UV-Vis-NIR absorption spectra of G3-DEHP (A) and G3-DMP (B) cast onto ITO/glass and biased in 0.5 M aqueous NaCl/H₂O. Spectra are reported every 0.2 V. Potentials are reported vs. Ag/AgCl. Spectra are scaled to give a maximal absorbance of 1.0 for the de-doped spectrum.
At intermediate potentials, the $\pi-\pi^*$ transition undergoes incremental bleaching as neutral species are converted to polaron and bipolaron. While bleaching, the $\pi-\pi^*$ transition also undergoes a gradual blue-shift, indicating that the remaining neutral chromophores in the system are increasingly distorted with increasing potential. For G3-DEHP, the doping process occurs through an isosbestic point at ~625 until a potential of +0.7 V is reached. Meanwhile the doping process of G3-DMP does not seem to show a single isosbestic point, perhaps suggesting a more complicated inter-conversion between neutral and charged species.

Throughout the doping process of G3-DEHP, the $A_{0.0}/A_{0.1}$ ratio of the neutral $\pi-\pi^*$ transition seems to decrease (Figure 6.2.3A). This behavior is distinct from the evolution of the fine structure for G3-DMP (Figure 6.2.3B), the other DMP copolymers reported in CHAPTER 5, the polar polythiophenes reported in CHAPTER 4, and rr-P3HT\textsuperscript{196,411} – all of which show an increasing $A_{0.0}/A_{0.1}$ ratio upon electrochemical doping.

A recent paper comparing field effect and electrochemical doping mechanisms of P3HT in electrolyte gated transistors reported that an increasing $A_{0.0}/A_{0.1}$ upon doping is associated with electrochemical charging, while decreasing $A_{0.0}/A_{0.1}$ is characteristic of field effect charging where only the polymer-electrolyte interface is doped.\textsuperscript{482} However, the optical changes occurring within the first few nanometers of electrostatically doped films are difficult to quantify. The authors did not use charge modulation spectroscopy, which is typically the preferred method for mapping polarons accumulating at organic semiconductor interfaces, choosing instead to use normal continuous wave UV-Vis absorption spectroscopy. Moreover, it was not unambiguously confirmed that the field
effect device involved only electrostatic charging and no ion penetration; this was an assumption based on the size of the electrolyte ions.

However, assuming this interpretation is valid, this result implies that differences in the evolution of $A_{0.0}/A_{0.1}$ may be related to how ion infiltration disrupts the arrangement of polymer chains in the film. Further studies are required to understand why the vibronic structure of G3-DEHP and G3-DMP evolve differently upon doping. Clearly, the spectral evolution for G3-DEHP is distinct from the other polymers and warrants additional investigation in a separate study.

6.2.3 Thin Film Microstructure

As a cursory characterization of microstructure, GIWAXS was performed on pristine G3-DEHP and G3-DMP films cast onto polished Si. These patterns on collected on pristine films, which are partially doped upon casting (Supporting Figure 6.4.5) and likely do not correspond to the microstructure of the electrochemically conditioned films.

The GIWAXS patterns of G3-DEHP and G3-DMP films exhibit relatively broad scattering, suggesting little long-range order and a relatively amorphous microstructure (Figure 6.2.4). Both feature a broad scattering halo at $q \approx 1.5 \text{ Å}^{-1}$ that is rather uniform across $\chi$, which is characteristic of isotropic powder-like diffraction. As explained previously, this arc is commonly attributed to “side chain interactions” in polythiophenes. It should be noted that many different interactions give rise to scattering at $q \approx 1.5 \text{ Å}^{-1}$ and the assignment of this arc is rather ambiguous.
Despite the similarities in the scattering patterns, some small differences can be discerned. In addition to the broad halo at $q \approx 1.5 \, \text{Å}^{-1}$, the line-cuts for G3-DEHP (Supporting Figure 6.4.6A) show an additional scattering feature at $q \approx 1.0 \, \text{Å}^{-1}$. Seeing as GIWAXS for the homopolymer of the DEHP unit showed a similar broad scattering peak at $q \approx 1.0 \, \text{Å}^{-1}$, it is possible that this scattering arises from a unique interaction from the ethylhexyloxy side chains in the DEHP unit.

![GIWAXS patterns for pristine films of A) G3-DEHP and B) G3-DMP coated on Si. Scattering intensities are normalized for film thickness and represented on a linear color scale. The different side chains structures for each polymer are shown.](image)

Both polymers also show a scattering feature at low q, which likely corresponds to the (100) peak arising from lamellar spacing. The lamellar spacing of G3-DEHP is slightly
larger than G3-DEMP by ~2 Å (Table 6.2.2)—a small difference that was reproduced in multiple samples. The bulkiness of the ethylhexyloxy side chain in G3-DEHP seems to cause an expansion of the lamellar spacing, despite these ethylhexyloxy side being shorter than the G3 side chains (8 atoms vs. 12 atoms).

The GIWAXS pattern of G3-DEHP also shows an overall lower scattering intensity. Meanwhile, G3-DMP has a slightly higher scattering intensity, which is characteristic of a greater fraction of diffracting species with long-range order. In the scattering pattern of G3-DMP, this increase in scattering intensity occurs chiefly in the out-of-plane direction around a $q_z$ of 1.55–1.60 Å$^{-1}$. Line cuts show an additional scattering peak at approximately $q_{xy} = 1.6$ Å$^{-1}$ (Supporting Figure 6.4.6B). Considering the positioning, intensity, and anisotropy of this feature, we attribute this signal to weakly scattering π stacks with $d_{(020)} = 4.0$ Å. Meanwhile, the line cuts of G3-DEHP show no scattering features resembling common π stacking signatures (Supporting Figure 6.4.6A).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$d_{(020)}$ (Å)</th>
<th>$d_{(100)}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3-DEHP</td>
<td>--</td>
<td>24.1</td>
</tr>
<tr>
<td>G3-DMP</td>
<td>3.9</td>
<td>22.5</td>
</tr>
</tbody>
</table>

All values represent average distances calculated from two separate films, cast and measured separately. Std. err. < 0.1 Å.
Based on these results, we conclude incorporating the minimally substituted DMP unit enhances intermolecular ordering. The corresponding reduction of side chain density gives rise to a weak π stacking scattering feature in G3-DMP (albeit with low coherence). A similar result was observed in CHAPTER 4, where the presence of an unsubstituted thiophene repeat unit resulted in enhanced solid-state ordering of EG-functionalized polythiophenes.

6.2.4 Neutron Reflectometry

As explained in the previous sections, the two materials under investigation (G3-DEHP and G3-DMP) differ in their side chain density and relative hydrophilicity. As a result, these materials behave differently upon doping, both in terms of their redox properties and potential-dependent absorption spectra. Though mostly amorphous, pristine films of G3-DEHP and G3-DMP exhibit subtle microstructural differences, as well. Considering these results, we expect that the physical properties of these films may also show distinct changes upon doping.

To answer the questions described in the introduction and gain more insight into the doping reaction, films of G3-DEHP and G3-DMP were studied using specular NR. These experiments were performed at the Spallation Neutron Source at Oak Ridge National Laboratory, as described in more detail in CHAPTER 2.7. Measurements were performed ex situ on dry pristine films, in situ on pristine films immersed in an electrolyte, and in situ on films electrochemically addressed in a three-electrode cell.
6.2.4.1 Model Development

As explained previously, the contrast in NR experiments arises from differences in the neutron scattering length density (SLD). The SLD depends on a material’s constituent atomic nuclei and overall density. Interpretation of NR data requires models that represent the structure and contrast of the sample.

Prior to beginning any measurements, it was therefore necessary to predict the experimental contrast and develop preliminary models. The SLD values of the substrate, electrode assembly, and electrolyte were calculated using the chemical formula and known density of the constituent materials (Table 6.2.3). For the PProDOT materials under study, an estimated SLD was calculated using the repeat unit formulae and assuming a density of \( \rho = 1 \text{ g cm}^{-3} \) (Table 6.2.3). For this calculation, the SLD of G3-DEHP is expected to be a bit lower than that of G3-DMP owing to the greater amount of hydrogen-1 (protium) in the repeat unit, which has a negative scattering length.

To measure the SLD of the two polymers, films of G3-DEHP and G3-DMP were spin-coated onto Si wafers and studied with neutron reflectivity. For each polymer, two separate films were coated and measured separately to ensure reproducibility. For these dry film measurements, the neutron beam was incident to the surface of the polymer film. The reflectivity profiles were fit to a four-layer model consisting of a Si substrate (or backing), a thin SiO₂ interlayer (representing the native oxide on the Si wafer), a polymer layer, and an air layer (also called the “fronting”). Details concerning the data fitting can be found in CHAPTER 2.7.3. Representative models and resulting fits for each dry film measurement are presented in Supporting Figure 6.4.7 and Supporting Figure 6.4.8. Both
polymer films could be modeled using a single layer with low interfacial roughness ($R_q < 10$ Å), indicating that the film is relatively homogeneous in composition and density throughout its depth. From these fits, the actual SLD of G3-DEHP was found to be slightly lower than what was estimated ($0.77 \times 10^{-6}$ vs. $0.83 \times 10^{-6}$ Å$^{-2}$), while the SLD of G3-DMP was nearly 50% greater than the estimated value ($1.17 \times 10^{-6}$ vs. $0.86 \times 10^{-6}$ Å$^{-2}$). Because the elemental composition of the polymers was separately confirmed by elemental analysis, we infer that the actual densities between the two polymers are different, with the density of the G3-DEHP film being slightly less than 1 g cm$^{-3}$ and the density of the G3-DMP film being slightly higher than 1 g cm$^{-3}$.

For NR studies performed in situ while biasing the films in an electrochemical cell, Au-coated Si wafers were used as the underlying working electrodes (WEs). The reflectivity patterns of the bare electrodes were recorded in ambient conditions with the beam incident to the Au surface. Data were fit to a four-layer model to extract the thickness and SLD of each layer in the WE substrates (Supporting Figure 6.4.9 and Supporting Figure 6.4.10). Given the similar SLDs of the Cr adhesion layer and the silicon oxide layer, there was not sufficient contrast between these materials to model them as two separate layers. Accordingly, the Cr and SiO$_2$ were modeled as a single layer.

Films of G3-DEHP and G3-DMP were spin-coated onto the Au-coated WEs. As with the previous dry sample measurements, the reflectivity profiles of these samples were recorded with the neutron beam incident to the polymer film. The reflectivity patterns were fit to a multi-layer model, as presented in Supporting Figure 6.4.11 and Supporting Figure 6.4.12. Consistent with the earlier measurements of films cast onto bare Si substrates, both polymers could be fit with a single layer and were found to have SLDs similar to those
found in the initial measurements. The thickness, SLD, and interfacial roughness extracted from these models was used as a baseline for comparing the volumetric and interfacial changes that occur upon doping.

Table 6.2.3 – SLD values for different materials used in the NR experiments. Calculated SLDs were obtained using the chemical formula and known density of the material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated SLD ($10^{-6}$ Å$^{-2}$)</th>
<th>Measured SLD ($10^{-6}$ Å$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3-DEHP</td>
<td>0.83$^a$</td>
<td>0.77</td>
</tr>
<tr>
<td>G3-DMP</td>
<td>0.86$^a$</td>
<td>1.17</td>
</tr>
<tr>
<td>H$_2$O(l)</td>
<td>-0.56</td>
<td>-</td>
</tr>
<tr>
<td>D$_2$O(l)</td>
<td>6.36</td>
<td>-</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.84</td>
<td>-</td>
</tr>
<tr>
<td>Au</td>
<td>4.50</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>3.10</td>
<td>-</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>3.20</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>2.07</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$) Calculated from repeat unit formula and assumed density of 1 g cm$^{-3}$.

Note that only measured SLD values are reported for the two polymers, as their density was not yet known.

6.2.4.2 Contrast Matching

As described previously, the SLD of different components in a system can be tuned by isotopic substitution. When the SLD of one material is tuned to match the SLD of another material in the sample, the contrast between the two phases is lost, and both materials behave as a single continuous phase. These so-called “contrast matching”
strategies allow for certain phenomena to be isolated and probed separately. Many contrast matching approaches involve incorporating some amount of deuterated material into a sample to modify its SLD. In these experiments, the use of an aqueous electrolyte allows for the SLD of the solvent to be tuned by mixing different ratios of H₂O/D₂O in the solution.

In order to study the swelling and ion uptake behavior of the PProDOTs, two different NR contrast matching schemes were attempted. By matching the SLD of the H₂O/D₂O electrolyte solvent to the NaCl salt, the electrolyte has a single SLD that is distinct from the polymer. The contrast between the electrolyte phase and polymer phase will result in neutron reflection at the polymer-electrolyte interface. Upon doping the film, ions and solvent will penetrate the film. The SLD of the polymer layer will change according to the amount of electrolyte in the polymer, resulting in different contrast. Moreover, variations in the thickness of the polymer film and the roughness of the polymer-electrolyte interface will manifest in the reflectivity pattern as variations in the size and dampening of the Kiessig fringes. This contrast matching approach, depicted schematically in Figure 6.2.5A, allows us to quantify the thickness and roughness changes upon doping.

Importantly, the extent of electrolyte uptake by the PProDOT films may be evaluated at a qualitative level only. When studying a simple two-component mixing process NR, the relative amount of each component can be calculated from a mass balance using the SLD of the mixed phase. However, for systems studied here, such analysis cannot be performed because the composition of the electrolyte inside and outside the film are not identical.
Figure 6.2.5 – Schematic depiction of contrast matching schemes attempted in NR studies showing A) matching SLD of the H\(_2\)O/D\(_2\)O electrolyte solvent to the NaCl salt, and B) matching SLD of the H\(_2\)O/D\(_2\)O electrolyte solvent to the polymer. Panels depict the potential origin of NR contrast for the dry film in air (left), pristine film exposed to electrolyte (middle), and doped films containing ions (right).

In the second contrast matching method, the SLD of the H\(_2\)O/D\(_2\)O solvent may be tuned to match that of the neat polymer. Consequently, the polymer-electrolyte interface will not be discernable in the reflectivity profile, and these two layers form a semi-infinite backing relative to the incident neutron beam. However, as the film becomes enriched with electrolyte ions, it is conceivable that new interfaces could appear in the reflectivity profile, depending on the depth profile of ions and any interfacial ion accumulation. In this scheme, any change in the polymer SLD can be attributed to ions exclusively and not solvent, seeing as there is not contrast between the polymer and solvent. Therefore, this contrast matching scheme (SLD\(_{\text{Solvent}}\) = SLD\(_{\text{Polymer}}\), Figure 6.2.5B) is designed to shed light on the ion distribution in the bulk of the film.
6.2.4.3 **Experimental Design**

For measurements performed in a three-electrode cell, each polymer-coated WE was assembled in a three-electrode cell with a Pt counter electrode (CE) and an Ag/AgCl reference electrode (RE). A description of the cell, along with a schematic depiction of the assembly, can be found in CHAPTER 2.7. The cell was filled with an aqueous electrolyte of 0.5 M NaCl. Dry sample measurements were performed with an upright geometry with the neutron beam incident to the top of the sample. For samples performed in the electrochemical cell, the geometry of the experiment was inverted such that the neutron beam was incident to the underlying Si substrate of the WE. Therefore, the ordering of the layers in the model were inverted. A schematic of the cell geometry is shown in Figure 6.2.6. Additional experimental details regarding data collection and processing can be found in CHAPTER 2.7.2.

![Diagram of three-electrode cell used for in situ NR studies](image)

**Figure 6.2.6** – Diagram of three-electrode cell used for *in situ* NR studies, showing inverted sample orientation with incident neutrons incident to the bottom of the cell. Changes in polymer characteristics, such as thickness (Δd) and scattering length density (ΔSLD), are depicted, along with the working, counter, and reference electrodes (WE, CE, and RE, respectively).
To answer question (i) posed in the introduction, which concerns the passive uptake of electrolyte, the reflectivity patterns of both films were recorded after filling the cell with the electrolyte and exposing the sample to the solution for 90 min. Question (ii) presented earlier in the introduction relates to the structural and interfacial consequences of the electrochemical conditioning process. The effect of the electrochemical conditioning or “break-in” process was evaluated by subjecting the films to ten doping/de-doping CV cycles. Next, the reflectivity profiles of the samples were recorded under potentiostatic conditions while applying a continuous de-doping potential (0.0 V for G3-DEHP, -0.4 V for G3-DMP) to study any potential irreversible changes in the film structure that occurred during break-in. Evaluation of the active, doping-induced swelling and electrolyte uptake (question (iii)) was accomplished by performing in situ NR studies incrementally at different potentials throughout the doping process. For these studies, films were held at potentiostatic conditions to drive the polymer into a partially or fully doped state.

These experiments were performed using H$_2$O/D$_2$O mixtures necessary for the contrast schemes presented in Figure 6.2.5. Excellent NR data was acquired for the contrast scheme presented in Figure 6.2.5A (SLD$_{\text{Solvent}}$=SLD$_{\text{Salt}}$), which were designed to monitor thickness, roughness, and roughness. However, the contrast scheme designed to selectively study ion accumulation (SLD$_{\text{Solvent}}$=SLD$_{\text{Salt}}$, Figure 6.2.5B) yielded reflectivity patterns that could not be fit to physically realistic models, perhaps due to an experimental issue. Accordingly, only results from first contrast matching scheme (Figure 6.2.5A, in SLD$_{\text{Solvent}}$ = SLD$_{\text{Salt}}$ ≈ $2.8 \times 10^{-6}$ Å$^{-2}$) were analyzed and will be discussed in the following section.
6.2.4.4 Physical Behavior of G3-DEHP

To study the passive electrolyte uptake and swelling behavior of G3-DEHP, NR was performed on a pristine spin-coated film in air and after immersing in the aqueous 0.5 M NaCl electrolyte. For evaluating the potential-dependent volumetric and interfacial changes, *in situ* NR was performed while applying three different electrochemical potentials to the same film of G3-DEHP. As illustrated in Figure 6.2.7A, these potentials correspond to different doping levels/oxidation states. When biasing at 0.0 V (which is below the $E_{ox}$ of G3-DEHP), the characteristics of the de-doped, broken-in polymer may be studied. Reflectivity profiles were also recorded while biasing the film at +0.3 V (corresponding to a partially doped state immediately, after $E_{ox}$) and at +0.8 V (corresponding to the most highly doped state).

The raw reflectivity curves for the G3-DEHP sample at every condition are shown in Figure 6.2.7B. The large periodic Kiessig fringes correspond reflection interference from the 30-nm Au electrode layer underneath the polymer film. The finer Kiessig fringes superimposed on the Au pattern represent the reflection interference from the polymer film. These reflectivity patterns were fit to multi-layer models, as described in CHAPTER 2.7.3. The reflectivity models and associated fitting parameters for these patterns are presented in Supporting Figure 6.4.11 and Supporting Figure 6.4.13 through Supporting Figure 6.4.16. The model was used to extract the thickness (d), SLD, and roughness ($R_q$) of each layer in the heterostructure. For the various conditions tested, the thickness and SLD values for the G3-DEHP film are presented in Figure 6.2.7C.
Upon exposure to the electrolyte, G3-DEHP undergoes a moderate change in thickness from approximately 173 nm to 188 nm. This result suggest that G3-DEHP swells slightly when immersed in the electrolyte, without the application of a bias. This change manifests in a narrowing of the fine Kiessig fringes in the NR curve (Figure 6.2.7B). The increase in the “magnitude” of the Kiessig fringes is due to a change in the contrast between the two configurations.

The passive swelling of G3-DEHP is consistent with behavior observed for polythiophenes using EQCM-D and ex situ X-ray methods. The fact that this process can be monitored by NR, as well, is a promising result.

When exposed to the electrolyte, the SLD of G3-DEHP increase from $0.77 \times 10^{-6}$ Å$^2$ to $0.90 \times 10^{-6}$ Å$^2$. Because SLD of the electrolyte is greater than the neat polymer (Table 6.2.3), the increased SLD of G3-DEHP suggests that electrolyte is being incorporated into the film. This further supports the notion that G3-DEHP swells passively when immersed in aqueous media. Because the reflectivity data could be modeled using a single layer representing the polymer phase, we conclude that the distribution of electrolyte in the film is relatively uniform throughout the depth of the film.

It should be noted that the diffusion of ions and solvent cannot be separated with the contrast scheme used in these experiments. Accordingly, we cannot unambiguously describe the relative enrichment of Na$^+$, Cl$^-$, or H$_2$O/D$_2$O in the G3-DEHP film upon swelling. Here, we assume that the change in SLD resulting from passive swelling is the result of both ions and solvent incorporation, whereas active swelling may be predominantly determined by chloride ions and solvent.
Figure 6.2.7 – A) CV of G3-DEHP in NaCl/H$_2$O showing potentials used for *in situ* NR. B) Raw NR data for G3-DEHP film under different conditions, offset for clarity. C) Thickness (d) and SLD of G3-DEHP extracted from fitting of data in (B).
After electrochemically conditioning and de-doping, the structure and composition of G3-DEHP appears to be slightly changed. The thickness of the polymer film is modestly increased to 202 nm, while the SLD of the film increases by 10%. In sum, the break-in effect for G3-DEHP does not seem to substantially influence film thickness or composition.

Further increasing the potential to +0.3 V and +0.8 V is associated with increases in film thickness to 216 and 223 nm, respectively (Figure 6.2.7C). Again, these changes in film thickness can be qualitatively seen by the narrowing of the Kiessig fringes in each successive NR pattern. While rather small, this growth in film thickness represents a consistent trend with every potential step, suggesting that the film is swelling upon doping. Again, the swelling is accompanied by an increase in the SLD of the G3-DEHP layer, which suggests increased electrolyte uptake by the film.

In the reflectivity pattern recorded at +0.3 V, which corresponds to a partially-doped state, the polymer Kiessig fringes appear to be dampened, especially at higher q (Figure 6.2.7B). This causes the overall scattering profile to resemble the characteristic evolution of Fresnel reflectivity ($R \propto q^{-4}$) and usually represents increased interfacial roughness. Such interfacial roughness is no longer evident in the reflectivity pattern corresponding to the fully doped state (+0.8 V). This observation suggests that at intermediate doping levels, the G3-DEHP/electrolyte interface becomes increasingly rough or diffuse. This will be discussed at greater length in a subsequent section (CHAPTER 6.2.4.6).
6.2.4.5 Physical Behavior of G3-DMP

Like the experiments described for G3-DEHP, NR was performed on G3-DMP after immersing in an electrolyte to study the extent of passive swelling. Given the different redox properties of G3-DMP, *in situ* NR was performed while applying four different electrochemical potentials. First, the reflectivity profile was recorded while biasing the film at -0.4 V, which corresponds to a de-doped, electrochemically conditioned state. Next, NR was performed while biasing in the film at 0.0 V. As shown in Figure 6.2.8A, this potential represents a partially doped state immediately after the first oxidation process. A subsequent NR experiment was performed while biasing the film at +0.6 V, which corresponds to a potential immediately after the second oxidation process (Figure 6.2.8A). To investigate the properties of the fully doped polymer, NR was performed while biasing the G3-DMP film at +0.8 V.

Figure 6.2.8B shows the raw reflectivity curves for G3-DMP sample at every condition tested, both in and outside of the electrolyte solution. As described before, the large periodic Kiessig fringes for G3-DMP correspond to reflection from the underlying Au electrode layer. Reflectivity from the thicker G3-DMP film (d = 95 nm) is represented by the finer superimposed Kiessig fringes. NR models used to extract the thickness, SLD, and roughness of each layer in the heterostructure are presented in Supporting Figure 6.4.12 and Supporting Figure 6.4.17 through Supporting Figure 6.4.21. The thickness and SLD values for each reflectivity study of G3-DMP are presented in Figure 6.2.8C.
Figure 6.2.8 – A) CV of G3-DMP in NaCl/H$_2$O showing potentials used for in situ NR. B) Raw NR data for DMP film under different conditions, offset for clarity. C) Thickness (d) and SLD of DMP extracted from fitting of data in (B).
Like G3-DEHP, G3-DMP undergoes passive swelling uptake upon exposure to the aqueous electrolyte. The film thickness increases from 95 to 112 nm, corresponding to roughly a 20% change. A proportional increase in the SLD of the polymer is observed (1.16×10^{-6} to 1.42×10^{-6} Å^{-2}, Figure 6.2.8C). The electrochemical conditioning of G3-DMP results in significant increases in the film thickness and SLD, as shown in the narrow Kiessig fringes in the -0.4 V pattern (Figure 6.2.8B). This break-in is associated with a 56% increase in film thickness relative to the dry state. The SLD of the G3-DMP also increases at -0.4 V, suggesting that that electrolyte irreversibly penetrates the film upon doping. Even though the film is fully de-doped at -0.4 V (see spectra in Figure 6.2.3B), the polymer still holds on to a fair amount of electrolyte. Based on the results of the NR studies performed at 0.0 V, the first redox process seems to be associated with a relatively small increase in film thickness (Δd=10 nm). Meanwhile, the second redox process (-0.4 V to +0.6 V) results in a thickness change of nearly 50 nm. Because the de-doped film is already enriched with electrolyte (as shown by NR studies performed at -0.4 V), it is possible that this imbibed electrolyte facilitates the first doping processes, which minimizes the need for further swelling at 0.0 V. This concept will be revisited in the following chapter.

When biasing G3-DMP to +0.8 V, the fine Kiessig fringes arising from reflection from the polymer are no longer clearly visible in the reflectivity pattern (Figure 6.2.8C). This could be due to several potential phenomena: (i) If the film swells beyond a thickness of ~250 nm, reflection from the polymer-electrolyte interface will no longer be evident in the NR pattern. Due to experimental limitations, neutrons reflected at interfaces beyond than 300 nm above the Si surface are not detectable. (ii) If the polymer-electrolyte interface were exceedingly rough, the Kiessig fringes may be dampened to such an extent that they
are not visible even at low q. (iii) Finally, if the polymer were to become enriched with so much electrolyte that its SLD became similar to that of the electrolyte, then contrast would be lost between the polymer and electrolyte phases. Here, it seems as though explanations (i) and (ii) are most influential.

Because the low-q region of NR data is the most sensitive, plotting the NR profile on a log-log scale may allow for subtle reflectivity features to be discerned. As shown in Supporting Figure 6.4.21D, weak Kiessig fringes corresponding to the G3-DMP layer can be seen in the log(R) vs. log(q) plot. Unlike the other data sets, this pattern could not be fit with a single layer for the polymer phase. This suggests that there is a non-uniform SLD profile across the depth of the film at the highest doping level. The polymer phase was then split into two separate reflectivity layers, and an optimized model was obtained (Figure 6.2.9A). Based on this model, the properties of G3-DMP film can be best described by a ~6 nm thick layer at the polymer-electrode interface with a higher SLD (1.97 × 10^{-6} \text{ Å}^{-2}) and a second, thicker layer with a lower SLD representing the rest of the polymer (d=250 nm, SLD = 1.65 × 10^{-6} \text{ Å}^{-2}).

While acknowledging the speculative nature of this fit, we note that the 6 nm layer at the polymer-electrode interface is consistent with the formation of an ion-rich double layer at the polymer-electrode interface. The increased film swelling and porosity with higher doping levels may permit the accumulation of excess ions at the interface. The overall decrease in the SLD of the bulk polymer at +0.8 V (SLD = 1.65 × 10^{-6} \text{ Å}^{-2} vs. 1.95 × 10^{-6} \text{ Å}^{-2} at +0.6 V) is not in line with expectations, considering the higher SLD of the electrolyte phase. However, one must also consider the fact that the chloride and sodium are transported into the film separately. So, while enrichment with chloride (SLD ≈ 5.22 ×
$10^{-6} \text{ Å}^2$) would result in the expected increase in SLD, incorporation of sodium ions (SLD $\approx 0.92 \times 10^{-6} \text{ Å}^2$) may lower the SLD. So, perhaps at high doping levels, transport of both species is occurring, as opposed to primarily chloride transport. However, considering the relatively poor resolution of this reflectivity pattern, this interpretation is rather speculative. Additional studies are required to quantitatively analyze the changes in the film structure for G3-DMP at +0.8 V.

However, without even fitting this data to a model, it is clear that the thickness and/or interfacial roughness of G3-DMP underwent a substantial change between +0.6 V and +0.8 V. This is evident by the overall loss of resolution and the dampening of the Kiessig fringes, especially at high q. So, from a qualitative perspective, we can still conclude that G3-DMP swells to a greater thickness with more interfacial roughness/diffuseness when the potential is increased to +0.8 V. This observation is rather interesting, seeing as there is relatively minimal spectral change occurring within this potential window (Figure 6.2.3B).

6.2.4.6 Comparison of Volumetric and Interfacial Changes

The *in situ* NR studies show that both G3-DEHP and G3-DMP experience changes in volume and composition upon doping. However, much like many of their other properties, the extent of passive and active swelling in these materials depends heavily on the polymer structure. Figure 6.2.9A shows the overall change in film thickness experience by both polymers under different conditions. Upon passive exposure to the electrolyte, polymer G3-DMP swells over twice as much as G3-DEHP (18% vs. 8% increase in thickness), despite seeming to have greater density and more ordering in the solid state.
The relative hydrophobicity of the two materials may explain the differences in passive swelling that occurs prior to doping, with the more hydrophobic G3-DEHP swelling to a lesser extent.

Figure 6.2.9 – A) Swelling of G3-DEHP and G3-DMP reported as a percentage change in thickness (%Δd) relative to the thickness of the pristine dry film. B) Polymer-electrolyte interfacial roughness (R_q) of G3-DEHP and G3-DMP. Thickness and roughness values were extracted from the fitted reflectivity profiles. Dashed line corresponds to electrochemical conditioning.
For both materials, exposure to the electrolyte solution also results in a slight increase in the polymer-electrolyte interfacial roughness (Figure 6.2.9B). Polymer G3-DEHP, which is functionalized with alternating polar and non-polar side chains, shows greater interfacial roughness than G3-DMP. Potentially, this increased interfacial roughness could correspond to heterogeneous swelling across the film, depending on the relative surface composition of polar and non-polar groups. In reflectivity experiments, a physical “rough” interface cannot be distinguished from a diffuse interface. Therefore, without further experimentation, the exact nature of the interfaces cannot be precisely determined.

The electrochemical conditioning process seems to have distinct effects on each polymer. After ten doping/de-doping cycles, the thickness of G3-DMP is permanently increased by over 50%, and the SLD is also substantially increased (Figure 6.2.8C). Meanwhile, the thickness of G3-DEHP is only increased by 16% relative to the dry film thickness (Figure 6.2.9). This suggests that G3-DMP traps more electrolyte during the break-in process. In addition, the interfacial roughness of G3-DMP is twice that of G3-DEHP after break-in, reflecting that the outermost layer of G3-DMP is potentially better solvated than G3-DEHP. In the de-doped state, G3-DMP is enriched with a greater fraction of electrolyte than G3-DEHP. As discussed previously, the optical “break-in” of G3-DMP is a bit more substantial than the break-in for G3-DEHP (Supporting Figure 6.4.5). Together, these results suggest that the break-in of G3-DMP is associated with a greater structural reorganization than what is observed for G3-DEHP. Electrochemical conditioning of G3-DMP is associated with a unique type of rearrangement and solvent trapping that is not observed for G3-DEHP. Differences in the break-in effect are also
apparent by the SLD depth-profile for both polymers (Supporting Figure 6.4.22), which showcases the change in the position and roughness of the polymer-electrolyte interface upon conditioning.

Seeing as the de-doped film of G3-DMP is imbibed with more electrolyte and has a more solvated interface, it seems to adopt a more “open,” hydrated, and porous film structure that is amenable to ion transport. These differences, shown schematically in Figure 6.2.10, potentially could explain differences in the redox properties described earlier in CHAPTER 6.2.2. Given the hydrated and “pre-swollen” state of the de-doped film, G3-DMP can support rapid doping/de-doping with less diffusional limitation. The film of G3-DEHP, on the other hand, is less hydrated and less swollen in the de-doped state. Therefore, electrochemical doping of G3-DEHP requires substantial mass transport and becomes much more diffusion-limited at lower scan rates (Figure 6.2.1B).

Figure 6.2.10 – Schematic of films of de-doped G3-DEHP and G3-DMP after electrochemical conditioning, depicting a greater extent of electrolyte trapping and interfacial roughness/diffuseness for G3-DMP.
Upon increasing the potential, G3-DMP undergoes two distinct oxidation processes. As explained previously, the first oxidation wave is usually ascribed to the doping of “aggregated domains” of polymer or regions in the film with greater order.\textsuperscript{129,255,257,380} The swelling during first oxidation process (-0.4 V to 0.0 V) is rather minimal, whereas the second oxidation process (0.0 V to +0.6 V) is associated with substantial swelling and a doubling of the original film thickness (Figure 6.2.9A).

The potential-dependent structural changes observed for G3-DMP provide insight into the origin of the fundamental electrochemical behavior of the material. When comparing the normalized CV traces of G3-DMP performed at different scan rates, the two redox processes show different behavior (Supporting Figure 6.4.23). The normalized peak current density for the first oxidation wave is relatively similar for all scan rates, suggesting it is not strongly diffusion controlled. This observation is consistent with the pre-swollen state of the de-doped film, which reduces the diffusional limitations of the first redox process. Potentially, the first redox process is less diffusion-limited because the film already contains many counter-ions. Meanwhile, the peak current density for the second redox process decreases at higher scan rates, suggesting this process is more strongly limited by diffusion. The NR experiments show that the second oxidation process also requires more substantial swelling and electrolyte uptake, which would be expected for a strongly diffusion-controlled process.

This result stands in contrast to an interpretation presented by Österholm et al. in a publication surrounding the redox properties of similar ProDOT-DMP copolymers.\textsuperscript{129} The authors report the opposite finding, stating that the first oxidation wave in the CV of the films actually shows a greater dependence on scan rate than the second wave. This
observation is used to support the hypothesis that the first redox process involves the selective doping of “aggregated domains,” seeing as ion transport into such aggregated domains would be tortuous and therefore more sensitive to scan rate. Considering that the study by Österholm et al. involved the use of PProDOTs with different side chains paired with an organic electrolyte, it is possible that particular polymer-polymer or polymer-electrolyte interactions play a role in dictating the “pre-swelling” behavior observed for G3-DMP. It is also worth noting that doping of particular domains does not necessarily mean that ion transport selectively occurs in these domains and leaves other domains unaffected. In fact, a recent study from 2018 suggested that electrolyte counter ions preferentially reside in unaggregated regions, even when stabilizing charges induced in aggregates.196

When comparing the overall volumetric changes at +0.8 V it is clear that G3-DMP swells substantially more than G3-DEHP at +0.8 V (Figure 6.2.9 and Supporting Figure 6.4.22). Even though G3-DMP is in a slightly higher oxidation state than G3-DEHP at +0.8 V (by spectroelectrochemistry, Figure 4.2.6), the overall differences in swelling seem much larger than the small difference in oxidation state. Thus, the side chain polarity and density have drastic effects on the swelling response of the polymer upon doping. G3-DMP, which overall is more polar and incorporates a minimally substituted comonomer, swells to a maximum thickness nearly three times its original size, whereas G3-DEHP swells only marginally. It is also worth considering that the initial density of the polymer film governs the extent of active swelling, as was reported for a family of EG-functionalized PTs by Schmode et al.403 G3-DMP, which is thought to be denser, may potentially have greater actuation capability than G3-OEtHex.
When biased to different doping levels, both PProDOT films undergo changes in their interfacial roughness (Figure 6.2.9B). The roughness of the G3-DMP-electrolyte interface increases consistently with increasing doping level, suggesting that the outermost region of the film becomes increasingly heterogeneous or diffuse. Considering the massive amounts of swelling observed for this material, a diffuse and highly solvated interface seems likely for this film.

In contrast to G3-DMP, the interfacial roughness of G3-DEHP did not increase continuously. G3-DEHP shows significant increase in roughness when held at an intermediate doping level (+0.3 V), which is approximately +0.1 V after the oxidation onset of the polymer. At this potential, the roughness of the polymer-electrolyte interface nearly doubled (Figure 6.2.9B). At the highest doping level (+0.8 V), however, the roughness subsides. Therefore, the interface of G3-DEHP seems to exhibit some amount of roughness that precedes the full electrochemical doping of the material. Presently, it is unclear whether this interfacial roughness is associated with heterogeneous swelling across the surface of the film or a compositional gradient, such as a moving front of ions penetrating film. Given the increased hydrophobicity of the polymer, perhaps this intermediate roughness is associated with a volumetric reorganization required to accommodate electrolyte. Alternatively, this intermediate roughness could represent an interfacial rearrangement of the polar and non-polar side chains to reduce to the energetic barrier associated with water uptake. Such interfacial reorganization processes are observed in the “flip-flop” behavior of lipid bilayers.483 Presently, the role of this intermediate increase in roughness is unclear, and further studies should be directed at better characterizing these potential-dependent interfacial processes.
6.3 Conclusions

This chapter utilizes a range of characterization techniques to develop a complete picture of the electrochemical doping of two aqueous-compatible ProDOT-based copolymers. Electrochemical studies show that the incorporation of the minimally substituted 2,2-dimethylProDOT (DMP) unit into the PProDOT backbone results in a lower oxidation onset, greater electroactivity, and less diffusion-limited behavior when compared to the analogue with longer ethylhexyloxy side chains. Spectroelectrochemistry and X-ray studies suggest that the DMP unit also confers a greater extent of intermolecular ordering, though both materials remain mostly amorphous in their as-cast state.

To shed light on the structural and compositional changes induced by electrochemical doping, \textit{in situ} neutron reflectivity studies are performed on the polymer films incrementally throughout the doping process. These experiments reveal that electrolyte irreversibly penetrates the polymer film, even prior to application of an electrochemical bias, as indicated by changes in film thickness and neutron scattering length density. After repeated cycling, the structure and composition of the films are permanently altered, with the DMP analogue trapping more electrolyte. Upon doping, the evolution of the swelling behavior and interfacial roughness depends on the repeat unit functionalization, with the DMP analogue showing greater electrolyte uptake and thickness change. The physical insights provided by the neutron reflectivity shed light on the diffusional limitations associated with the doping reaction. Such results demonstrate the importance of the hydration of the de-doped film in determining the final redox properties and ion transport behavior of the polymer film. This work sets a precedent for using neutron
reflectivity to directly study the potential-dependent volumetric and interfacial characteristics associated with the doping process to inform the design of high performing materials.

6.4 Supporting Figures

Supporting Figure 6.4.1 – Differential pulse voltammograms of (A) G3-DEHP and (B) G3-DMP in 0.5 M NaCl/H₂O, showing experimental data (solid lines) and tangents used for determination of E_{ox} (dashed lines).
Supporting Figure 6.4.2 – Cyclic voltammograms (v = 50 mV s\(^{-1}\)) showing electrochemical conditioning effect for films of G3-DEHP (A) and G3-DMP (B) on ITO/glass and cycled in 0.5 M NaCl/H\(_2\)O. Dashed lines correspond to the first CV trace of films as-cast. Solid lines correspond to the tenth CV trace, after conditioning.
Supporting Figure 6.4.3 – Cyclic voltammograms of G3-DEHP and G3-DMP films in 0.5 M TBAPF₆/PC after electrochemical conditioning (ν = 50 mV s⁻¹). Potentials are vs. Ag/Ag⁺ (Fc/Fc⁺ E₁/₂ = +65 mV).

Supporting Figure 6.4.4 – Potential-dependent C* for G3-DEHP and G3-DMP in degassed 0.1 M NaCl/H₂O, as determined by EIS performed under an argon blanket and normalized to the dry film volume. Note that the data for G3-DMP have been adapted from Figure 5.2.4
Supporting Figure 6.4.5 – UV-Vis-NIR absorption spectra showing electrochemical conditioning effect for (A) G3-DEHP and (B) G3-DMP films cast onto ITO/glass and cycled 10 times in 0.5 M NaCl/H$_2$O. Pristine spectra correspond to data for as-cast dry films prior to any treatment. Potentials for de-doped films are reported vs. Ag/AgCl. Absorption intensities are scaled to a maximum absorbance of 1.0 for the conditioned films.
Supporting Figure 6.4.6 – Sine corrected GIWAXS line cuts for A) G3-DEHP and B) G3-DMP with associated side chain structures.
Supporting Figure 6.4.7 – NR analysis of G3-DEHP on bare Si wafer in air. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.8 – NR analysis of G3-DMP on bare Si wafer in air. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.9 – NR analysis of bare Au-coated Si wafer that was used for G3-DEHP studies. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.10 – NR analysis of bare Au-coated Si wafer that was used for G3-DMP studies. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.11 – NR analysis of G3-DEHP on Au-coated Si wafer in air. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.12 – NR analysis of G3-DMP on Au-coated Si wafer in air. A) schematic of multi-layer model and fit parameters, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.13 – NR analysis of pristine G3-DEHP film on Au-coated substrate immersed in electrolyte, prior to any electrochemical conditioning. A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.14 – NR analysis of electrochemically condition G3-DEHP film on Au-coated substrate, immersed in electrolyte and held at a de-doping potential of 0.0 V vs. Ag/AgCl. A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.15 – NR analysis of electrochemically condition G3-DEHP film on Au-coated substrate, immersed in electrolyte and held at a de-doping potential of +0.3 vs. Ag/AgCl (slightly oxidized). A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.16 – NR analysis of electrochemically condition G3-DEHP film on Au-coated substrate, immersed in electrolyte and held at a de-doping potential of +0.8 vs. Ag/AgCl (highest oxidation state). A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (red circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.17 – NR analysis of pristine G3-DMP film on Au-coated substrate immersed in electrolyte, prior to any electrochemical conditioning. A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.18 – NR analysis of electrochemically condition G3-DMP film on Au-coated substrate, immersed in electrolyte and held at a de-doping potential of -0.4 V vs. Ag/AgCl. A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.19 – NR analysis of electrochemically conditioned G3-DMP film on Au-coated substrate, immersed in electrolyte and held 0.0 V vs. Ag/AgCl (after first oxidation wave). A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), and C) SLD depth profile extracted from fit.
Supporting Figure 6.4.20 – NR analysis of electrochemically conditioned G3-DMP film on Au-coated substrate, immersed in electrolyte and held +0.6 V vs. Ag/AgCl (after second oxidation wave). A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), C) SLD depth profile extracted from fit, C) Expansion of low-q region of panel (B) plotted on log-log scale for clarity.
Supporting Figure 6.4.21 – NR analysis of electrochemically conditioned G3-DMP film on Au-coated substrate, immersed in electrolyte and held +0.8 V vs. Ag/AgCl (highest oxidation state) A) Schematic of multi-layer model and fit parameters for run, B) reduced reflectivity data (blue circles) with fit (black line), C) SLD depth profile extracted from fit, C) Expansion of low-q region of panel (B) plotted on log-log scale for clarity.
Supporting Figure 6.4.22 – SLD plots resulting from fitting of neutron reflectivity data of A) G3-DEHP and B) G3-DMP immersed in 0.5 M NaCl under different conditions. The curves represent a one-dimensional view of the substrate-polymer-electrolyte heterostructure moving in the positive z direction from the substrate to the electrolyte phase. Gray arrow represents the changes associated with the electrochemical break-in.
Supporting Figure 6.4.23 – Scan rate dependence of CV for G3-DMP film drop-cast on a GC button electrode and cycled in NaCl/H_{2}O. The current density has been normalized to the scan rate to give a capacitance value.
6.5 Additional Experimental Details

Information regarding electrode/substrate preparation, solution coating, and electrolyte preparation can be found throughout CHAPTER 2.

Experimental details surrounding neutron reflectivity studies and sample preparation can be found in CHAPTER 2.2 and CHAPTER 2.7. In situ NR studies were performed using a Bio-Logic VSP controlled by EC-Lab software. All NR experiments were performed in ambient conditions with no degassing performed prior to measurements.

For CV and DPV presented in the main text, films were drop-cast on glassy carbon button electrodes \( (a = 0.07 \text{ cm}^2) \), unless otherwise noted. For drop-casting, polymers were dissolved in room-temperature chloroform overnight at a concentration of 4 mg mL\(^{-1}\). Identical masses of each polymers were drop-cast (four 1-μL aliquots, 4 μL total volume, 16 μg total polymer mass) onto the active area of the electrode. Aqueous CV and DPV studies were performed under an argon blanket using a Reference 3000 Gamry potentiostat/galvanostat/ZRA controlled with Gamry Framework 6.5 software.

For CVs recorded in 0.5 tetrabutylammonium hexafluorophosphate in propylene carbonate (TBAPF\(_6\)/PC) films were spray-cast onto ITO/glass from 4 mg mL chloroform solutions, as described in greater details in CHAPTER 2.2. For these studies employing an organic electrolyte, CV was performed on an EG&G Princeton Applied Research 273A potentiostat/galvanostat with CorrWare software using a Pt flag CE and an Ag/Ag\(^+\) reference electrode assembled in house (inner solution of 3 M AgNO\(_3\) in ACN).
Films for EIS and potential-dependent UV-Vis absorption spectroscopy were fabricated by blade-coating from chloroform solutions onto clean ITO/glass substrates. Blade coating parameters were identical to those described in CHAPTER 5.5.

EIS was performed under an argon blanket in a degassed solution of 0.1 M NaCl/H₂O after electrochemical conditioning, as described in 5.5. Extraction of C* from the EIS data was performed by fitting the low-frequency portion of the impedance spectra to R-CPE series circuits and normalizing the capacitance to the volume of the dry, dedoped film (see CHAPTER 2.3.4 and CHAPTER 5.5). For G3-DMP the EIS values represent the average measurements performed on 3+ different films, as adapted from data presented in CHAPTER 5. While EIS was performed in a 0.1 M NaCl electrolyte solution (vs. 0.5 M), the C* of CP films is independent of electrolyte concentration within this range,²⁹²,⁴⁸⁴ allowing for these results to be compared to other characteristics and properties.

UV-Vis-NIR absorption spectroscopy was performed using a Cary 5000 UV-Vis-NIR, as described in CHAPTER 2.4. Potential-dependent spectra were recorded under potentiostatic conditions in 100 mV increments. To ensure the polymer had reached steady-state, the film was held at a given potential for ~30 s until the current transients plateaued before recording the spectrum.

To prepare samples for GIWAXS, films were cast on polished Si wafers under conditions identical to those used for preparing EIS and spectroelectrochemistry samples. GIWAXS was performed at the Stanford Synchrotron Radiation Lightsource (SLAC National Accelerator Laboratory) at beamline 11-3. A beam energy of 12.7 keV was
employed and the incident angle of the measurement was approximately 0.13°. The sample
distance was approximately 250 mm. Scattering patterns were calibrated using a standard
sample of LaB₆. Data was processed and analyzed as described in CHAPTER 2.5.
CHAPTER 7. PERPSECTIVE AND OUTLOOK

Redox-active π-conjugated polymers have tremendous potential in a variety of emerging electrochemical technologies, including energy storage devices, biological sensors, and electrochromic displays. The research presented in this dissertation explores the materials design principles that govern the properties of two classes of π-conjugated polymers: poly(thiophenes) and poly(dioxythiophenes). Structural modifications to the parent backbone and side chain is shown to influence the fundamental electrochemical, optical, and physical characteristics of the materials. In addition, these structural changes may be leveraged to enhance metrics that are important for device performance, such as electrochromic contrast, capacitance, aqueous redox activity, and long-term stability. Beyond presenting new results and interpretations, this body of work also identifies areas that warrant further scientific investigation.

7.1 Bleaching and Coloration in Electrochromic Polymer Bends

CHAPTER 3 reported the development and characterization of various three-component electrochromic polymer blends that can transition between black and transmissive states with relatively achromatic intermediate states. When biasing the polymer films at intermediate potentials, the steady-state achromaticity of the transitional states can be tuned by incorporating alternative high-gap and low-gap components that transition between colored and colorless states within a similar potential window.

However, when applying a square wave bias to switch the film immediately from its black state to its transmissive state, controlling the intermediate coloration becomes much more difficult. In these cases, the transient chromaticity depends on the relative rates
of the electrochromic transition for all constituent chromophores and therefore becomes strongly dependent on electron transfer kinetics, mass transport phenomena, and the applied overpotential. This process is very difficult to engineer, as it involves the simultaneous and coupled transport of ions and electrons through depth of the polymer film. Ion and electron transport cannot be straightforwardly characterized and controlled as independent processes in materials where these transport processes are not physically separated. This especially applies to a multi-component system comprised of different conjugated polymers, each exhibiting distinct transport characteristics.

To better address these matters, further research is required to develop methods for identifying the rate-limiting step of the redox process and characterizing ion and electron transport processes separately. For instance, there are relatively few ways to directly measure ion transport in mixed-conducting conjugated polymers, and the methods that do exist are either disputed, not generalizable to all materials, or fail to provide absolute values of ion mobility.

In the case of multi-component systems, such as the electrochromic polymer blends presented in CHAPTER 3, differences in the relative rates of doping for each polymer are expected to result in substantial heterogeneity with respect to the amount of conducting (doped) and insulating (de-doped) chains in the film at any point in time. Therefore, the electron/hole transport required for doping a given film domain may be obstructed by the insulating, de-doped domains nearby. In this case, different approaches may be required to enhance the electron transport throughout the depth of the film.
It may be advantageous to partially separate the phases in which ion and electron transport occurs. For instance, incorporation of a small amount of a conducting additive may facilitate electron transport in these heterogeneous systems. The conducting additive may provide pathways to facilitate charge transport, resulting in an overall faster electrochromic transition where intermediate colors are less apparent. In the literature, these approaches have been demonstrated by the addition of carbon nanotubes. Such polymer-nanotube blends have also been shown to exhibit superior ion transport processes when compared to the neat polymer film, which is usually is thought to arise from morphological effects.485–487

When considering incorporating such additives into a film, one must ensure that the stability, color, and processability of the active electrochromic layer is not detrimentally affected. Potentially, this also could be accomplished by the incorporation of a small amount of an electron-rich poly(dioxythiophene) with an E_{ox} that is much lower than the other constituents so that the additive polymer is always conducting during the switching process. A poly(dioxythiophene) additive would be transparent, conducting, processable, and would not disrupt the phase behavior of the rest of the active layer.

In addition, the work in CHAPTER 3 chiefly focused on the intermediate states associated with the black-to-transmissive bleaching transition. In most of applications, the reverse transmissive-to-black coloration process is equally important to the ultimate device functionality. There is also ample opportunity to study the intermediate coloration upon application of the reverse bias, which may actually occur faster and with less apparent chromaticity due to the conducting nature of the polymers in their doped states.
Beyond electrochromism, multi-component blends of π-conjugated polymers could be used for other applications, as well. For instance, one could develop a system for the multi-stage release of charged cargo, such as drugs or neurotransmitters, from films comprised of different polymers with different redox potentials. In the case of p-type materials, this could be accomplished by doping the polymer film in an electrolyte solution comprised of the desired anion to “load” the cargo, then putting the material in a biological system and applying de-doping potentials to trigger cargo release. Unlike in CHAPTER 3, where the redox potentials of constituted polymers were designed to be similar for coordinated bleaching, electroactive materials for staged drug delivery should be designed with vastly different redox potentials so that the “dose” may be precisely dialed by the applied potential. This sort of stepwise, gradual delivery could have advantages over methods of electrochemical release, which can suffer from a "burst" of uncontrolled release immediately upon biasing.

### 7.2 Underlying Structure-Property Relationships in Redox-Active Polymers

The work presented in CHAPTER 4 demonstrated the drastic effect that side chain substitution pattern can have on the electrochemical and microstructure properties of conjugated polymers. Incorporation of an unsubstituted thiophene ring into the backbone of ethylene-glycol (EG)-functionalized polythiophenes resulted in greater capacitance, enhanced redox stability, and increased microstructural order—even when the relative electroactive fraction of the polymer film was reduced. Localizing the side chain density on one comonomer while leaving the other comonomers relatively less substituted appears to be an advantageous strategy for designing highly electroactive conjugated polymers for applications like OECTs and supercapacitors. A similar approach was recently
demonstrated by Moser at al., who showed that this “side chain re-distribution” approach can be used to yield high performing and stable materials without reducing the overall density of the side chains required for processsing.416

When comparing the effect of side chain substitution on the properties of aqueous-compatible poly(3,4-propylenedioxythiophenes) (PProDOTs) in CHAPTER 6, a similar result is found. Incorporation of the minimally substituted 2,2-dimethylProDOT (DMP) unit into the backbone results in a lower oxidation onset in both aqueous and organic media, greater electroactivity, and less diffusion-controlled redox behavior. The results of the neutron reflectivity study also reveal that the ProDOT with the DMP analogue also swells to a greater degree when compared to the polymer with long side chains on every ProDOT unit. Polar PProDOTs incorporating this DMP unit were further studied in CHAPTER 5, where they showed promising properties when used as active materials in aqueous OECTs.

The effects of these unsubstituted or minimally substituted “spacer” units may be inter- or intramolecular in origin. Inter- and intra-molecular effects can be very difficult to separate, especially since they can sometimes influence each other. Based on the UV-Vis-absorption spectra (and to a lesser extent the GIWAXS patterns) presented in CHAPTER 4 and CHAPTER 5, we have tentatively ascribed this effect to the enhanced inter-molecular interactions promoted by the spacer unit. These increased interactions between chains are thought to lower the oxidation onset and enhance the charge storage capacity by increasing the extent to which polaron can be delocalized two-dimensionally across chains. In the case of the polymers studied in CHAPTER 6, the greater inter-molecular ordering in the DMP polymer may also explain the more substantial “break-in” effect that is observed for this material.
Studies concerning the electrochemical and solid-state properties of ProDOT-EDOT (PE) copolymer series showcase an analogous effect arising from incorporating unsubstituted EDOT units into the backbone. Replacing highly substituted and side chain-rich ProDOT units with unsubstituted EDOT units results in enhanced capacitance and conductivity.\textsuperscript{102,120} This effect was to be due chiefly to intra-molecular in origin, arising from “\textit{steric hindrance from neighboring propylene bridges...that disrupt further planarization of quinoidal structures}”\textsuperscript{120} for polymers with increasing ProDOT fraction. However, computational results form a later study demonstrated that the through-space resonance stabilization between a biProDOT and biEDOT were roughly the same, indicating no such disruption in chain planarity is induced by the ProDOT unit itself.\textsuperscript{102} This paper goes on to state that differences between the PProDOT and ProDOT\textsubscript{2}-EDOT copolymer cannot be fully explained given the suite of data reported in this work.

Neither of these studies investigate the intermolecular interactions facilitated by the unsubstituted repeat unit, which based on the findings reported in this thesis, are non-negligible in determining the electrochemical properties of the active polymer. Related discussions surrounding the relationship between intermolecular ordering and redox properties were reported in early 1990s with the electrochemical characterization of poly(cyclopentadithiophenes).\textsuperscript{270} Here, modulation of the interchain spacing by side groups results in drastically different redox properties and capacitive behavior, which the authors attribute to “\textit{π dimerization}” of polarons.

With these concepts in mind, it is necessary to develop molecular descriptions of charge formation and stabilization in electrochemically doped polymers to predictably design active materials for redox applications. Charged states in \textit{π}-conjugated redox
systems remain relatively understudied, especially when compared to the ample amount of research surrounding charge formation and transport in OPVs and other solid-state applications. With the renewed interest in the electrochemical functionality of π-conjugated polymers, especially in the bioelectronics community, there is immense opportunity to pursue fundamental questions relating to the complex interplay of polymer-polymer, polymer-ion, and polymer-electrode interactions that exist in these redox systems.

While a rather immense undertaking for the field as a whole, a starting point for the PProDOTs presented in this thesis would involve fundamental photophysical studies to make better sense of the neutral and potential-dependent absorption line shape of the π-π* transition. As alluded to previously described in this thesis, the absorption line shape of the PProDOTs seems to arise from an interplay of polymer structure, side chain substitution and length, molecular weight, and aggregation properties, much like P3HT. However, unlike P3HT and other commonly studied conjugated polymers, significantly less is known are the photophysical behavior of PProDOTs. In part, this is because most PXDOTs are used in settings where subtle changes in the neutral state absorption spectra are not very important, such as in supercapacitors or in electrochromic displays (were small differences in line shape don’t usually change the perceived color or contrast).

As the field expands and new electrochemical applications for these mixed-conducting materials are discovered, it becomes increasingly important to understand charge carrier evolution, stabilization, and transport in these electron-rich materials. The absorption spectra of the charged states often show substantial but unexplained differences in their position, line shape, intensity, and potential dependence. Several recent studies
have begun evaluating the optical signatures of polarons a bit more thoroughly, but a lot remains to be explored with respect to electrochemically induced charges. To these ends, fundamental photophysical studies of neutral and charged states in PXDOTs could unlock a powerful toolset for understanding and predicting material behavior in redox applications.

### 7.3 Importance of Ordering in Mixed Conductors

For the EG-functionalized polythiophenes studied in CHAPTER 4, side chain substitution patterns that were associated with increased ordering (by UV-Vis and GIWAXS) were generally found to be associated with greater redox activity and stability. As described above, this difference was hypothesized to be the result of the unique intermolecular interactions facilitated by the unsubstituted thiophene ring in the polymer backbone. A similar, though less drastic, relationship between inter-molecular ordering and redox activity was hypothesized to explain the differences observed for the polymers studied in CHAPTER 6. In this chapter, the polymer that seemed to have greater inter-molecular ordering (G3-DMP) also seemed to swell more in response to electrochemical cycling—a result that emphasized how different types and extents of “ordering” can manifest across different length scales.

As discussed previously in this thesis (see CHAPTERS 4.2.4, 5.2.4, and 6.1.2), the role of ordering in the properties of redox-active \( \pi \)-conjugated polymers is not comprehensively understood. Depending on the particular system, various relationships have been hypothesized. Effective ion and electron transport usually require competing materials design criteria, with ion transport being favored in amorphous/disordered
systems and charge carrier stabilization and transport generally favored in more ordered systems. What is missing in this hypothesis is a delineation between the particular length scales and dimensionality of order that matter for these two processes. For instance, high mobility in conjugated polymers can be achieved through very short-range intermolecular order, as was reported for an indacenodithiophene-benzothiadiazole copolymer.\textsuperscript{316} From the body of work presented in this thesis, it is clear that some amount of ordering of the \( \pi \) system is beneficial for redox properties, but of course, there must be a point at which ordering becomes detrimental to ion transport and morphological stability. With this in mind, it would be useful to identify the critical length scale of ordering (and nature/directionality of such order) that will facilitate high doping densities and carrier transport without obstruction ion transport.

This concept was recently explored by Kim et al. who studied the properties and OECT characteristics of PPy films fabricated with varying amounts of a 4,4′-biphenyldisulfonic acid (BPDSA) “connector.”\textsuperscript{489} The BPDSA was added to increase the crystallinity and order in the material. At low degrees of crystallinity and crystallite size, increasing the amor in the PPy by increasing the amount of BPDSA resulted in greater doping levels, a twelve-fold increase in \( C^* \), and enhanced OECT performance. Intermediate levels of BPDSA resulted in a greater degree of crystallinity which facilitated carrier mobility without obstructing ion flow. However, a limit was reached at higher BPDSA loadings, where large crystallites obstructed ion flow (Figure 7.3.1). Studies such as these, which systematically decouple microstructural factors from other variables influencing properties, are useful for identifying optimal regimes of performance.
While there have been many attempts to replace PEDOT:PSS as an active material for OECTs, it is possible that the dual-phase nature of PEDOT:PSS is actually quite beneficial for enabling effective ion and electron/hole transport. The general hypothesis is that ion transport occurs predominantly in the PSS phase, while hole transport occurs in the PEDOT-rich domains. In fact, recent studies have posited that the electrochemical characteristics of PEDOT:PSS can be explained by considering capacitive charging of the internal interfaces of PEDOT-rich and PSS-rich domains. This type of two-phase system may be optimal ensuring facile ion transport without disrupting carrier mobility. For this reason, it may be worthwhile to pursue such dual-phase materials with separate ion- and electron/hole- conducting phases. This could be accomplished by blending π-conjugated polymers with ion conducting polymers, other conjugated
polymer/polyelectrolyte complexes, or developing block copolymers with conjugated and non-conjugated blocks, as discussed in a recent review.\textsuperscript{18}

When considering these two-phase systems, it is interesting to revisit the “pre-swelling” behavior identified using neutron reflectometry in CHAPTER 6. The polymer G3-DMP showed substantial electrolyte uptake and permanent swelling (>50% thickness increase) after electrochemical conditioning, even when de-doping the polymer. The excess electrolyte in the film is not the result of trapped polarons, as shown by the potential-dependent absorption spectra. Considering that the film does not undergo much swelling with the first oxidation process, it seems as though the excess electrolyte incorporated into the polymer facilitates ion transport while minimizing structural reorganization of the film. In this sense, it is possible that G3-DMP might effectively behave as a two-phase system of polymer and electrolyte. This may be why the polymer seems to be an effective mixed conductor.

7.4 Factors Determining Stability in Aqueous Electrolytes

The stability of π-conjugated polymers upon repeat doping/de-doping cycles is of critical importance for any practical application. In the biological applications, long-term stability can be particularly difficult to achieve given the presence of proteins that can adsorb to the active layer and other species that may induce electro(chemical) degradation. To address the first point, the incorporation of EG-based side chains onto the backbone (which is a common strategy for imparting aqueous redox activity) may actually the physical enhance stability, as PEO and related oligomers are commonly used to resist non-specific protein adsorption onto surfaces.\textsuperscript{490,491} Regarding the chemical stability associated
with the electrolyte, the presence of molecular oxygen, reactive oxygen species, and peroxides which may react with the polymer active layer and accelerate chemical degradation. In addition, biological media is rich with potential nucleophiles (water, chloride, cystine, etc.) that may react with the conjugated polymer.

As explained previously, degradation of polyheterocycles in the presence of nucleophiles is thought to occur through nucleophilic attack of the doped polymer at unsubstituted β positions of the backbone, resulting in loss of conjugation. Therefore, steric protection of β position with alkyl or alkoxy groups is a common strategy for improving the electrochemical stability of polyheterocycles.

The stability tests performed on the aqueous-compatible polymers in this dissertation show results contrary to this long-standing hypothesis. For the polythiophenes presented in CHAPTER 4, the polythiophenes with more unsubstituted or “open” β positions show superior redox stability upon repeat cycling. Even when compared to the PProDOTs in CHAPTER 5, which are substituted at both β positions of the thiophene ring and are therefore usually considered to be more stable, the polythiophenes from CHAPTER 4 show similar or even enhanced stability.

This result was very unexpected, and several possible reasons for this have been discussed in the respective chapters. Perhaps the most likely explanation lies in the fact that many instances of degradation by electrochemical “over-oxidation” occur at potentials outside the electrochemical window of water. When studying electrochemical stability in aqueous electrolytes, it is possible that these over-oxidation mechanisms play less of a role in electrochemical degradation owing to the narrow working potential of water.
Considering these results, it is necessary to re-examine the factors that govern the electrochemical stability of conjugated polymers specifically in aqueous electrolytes, which may involve pathways that have not yet been identified.

7.5 Configurational Effects in OECT

As discussed at extensively in this thesis, there are still open questions regarding the properties that are most important for determining OECT performance. Moreover, the field is continuously improving its description of device behavior and identifying new complications that may convolute device behavior. These various complexities are outlined in CHAPTERS 1.3.2, 2.3.4.4, and 5.2.5.

In particular, the results presented in CHAPTER 5 highlighted how differences in the device configuration and geometry can result in very different apparent performance metrics, even for the same materials. In particular, the effects of contact resistance and thickness dependence were highlighted. Contact resistance effects depends on a number of factors, including the W/L ratio of the channel, the particular polymer structure, the doping level, and the nature of the polymer-electrode interface. Accounting for it would involve a very rigorous and compressive approach that, while perhaps tedious, would yield incredibly valuable and representative descriptions of materials. Moreover, the thickness-dependence of performance must be addressed, both with respect to the effects that manifest from “over-coating” electrodes as well as depth-dependent properties in microstructure and transport.

While the field becomes increasingly aware of these issues, it is worth considering whether device measurements are really the most optimal way to benchmark OECT active
materials and describe transport in electrochemically doped conjugated polymer films. In sum, there is a great need to refine the metrology used for characterizing carrier transport in electrochemically doped polymers.
APPENDIX

A.1 Synthesis and Structural Characterization of Polymers G2-DMP and G4-DMP

Polymers G2-DMP and G4-DMP (reported in CHAPTER 5) and associated monomer precursors were prepared by Brandon T. DiTullio (GT). The synthetic procedures and structural characterization of these materials have been kindly documented by DiTullio and provided herein.

A.1.1 Materials and Methods

All reagents were purchased and used as received from commercial suppliers: Pd(OAc)$_2$ (99.9%, Acros Organics), pivalic acid (99%, TCI America), K$_2$CO$_3$ (anhydrous, VWR), diethylene glycol monomethyl ether (98%, Aldrich), triethylene glycol monomethyl ether (98%, TCI America), tetraethylene glycol monomethyl ether (98%, Acros Organics), N-bromosuccinimide (99% NBS, Sigma Aldrich), NaH (90%, Sigma Aldrich), and diethyldithiocarbamic acid diethylammonium salt (97%, TCI America). Dimethylacetamide (HPLC grade DMAc, VWR) was degassed by argon bubbling and stored over molecular sieves prior to use. Silica (60 Å porosity) used for column chromatography was purchased from Sorbent Technologies, Inc. $^1$H NMR and $^{13}$C NMR spectra for all monomers and molecular precursors were acquired on a Varian Mercury Vx 300 MHz instrument using CDCl$_3$ as the solvent at 25 °C. $^1$H-NMR spectroscopy of polymers G2-DMP and G4-DMP was performed using a Bruker AVIIII-400 MHz instrument with CDCl$_3$ as the solvent at 50 °C. The residual CHCl$_3$ peak was used as a reference for all reported chemical shifts ($^1$H: $\delta = 7.26$ ppm, $^{13}$C: $\delta = 77.16$ ppm). Gel
permeation chromatography (GPC) was performed using a chloroform Tosoh EcoSEC GPC instrument with an RI detector to determine the number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and dispersity ($D$) relative to polystyrene (PS) standards. GPC was performed at 40 °C. Elemental analysis was conducted by Atlantic Microlab Inc.

Compound (1) (ProDOT(CH$_2$Br)$_2$) was prepared using published procedures$^{100}$ and characterized by $^1$H-NMR and GC-MS analysis. Similarly, compound (3) (DMP-Br$_2$) was synthesized and purified according to published procedures$^{129,132}$ and characterized by $^1$H-NMR and GC-MS.

A.1.1 Preparation of Polymer G2-DMP

A.1.1.1 Synthesis of Compound (2)

Scheme A. 1 – Synthetic route toward compound (2).

Under an inert atmosphere of argon, neat sodium hydride (NaH, 0.631 g, 26.31 mmol, 3 equiv.) and a stir bar were added to a flame-dried 250 mL round bottom flask. Next, compound (1) (3.00 g, 8.77 mmol, 1 equiv.) and 100 mL of anhydrous $N$,$N$-dimethylacetamide (DMAc) were mixed separately and added to the flame-dried 250 mL round bottom flask via cannulation. The resulting mixture of NaH, compound (1), and
DMAc was purged with argon while stirring at room temperature for 30 min. Diethylene glycol monomethyl ether (3.16 g, 26.31 mmol, 3 equiv.) was then added dropwise to the reaction mixture while stirring. After addition, the reaction mixture was heated to 120 °C and allowed to stir vigorously for 16 h under positive argon pressure. Once the reaction was complete, the mixture was cooled to ambient temperature, extracted with dichloromethane (DCM), and washed with deionized water. The organic layer was then washed repeatedly with brine. The organic phase was collected and subsequently concentrated under reduced pressure by rotary evaporation and purified by column chromatography using a 4:1 mixture of ethyl acetate (EtOAc) and hexanes as a mobile phase. The product, compound (2), was obtained as a clear oil with a faint yellow hue in a 68% yield (2.52 g). $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C), δ (ppm) 6.44 (s, 2H), 4.02 (s, 4H), 3.70-3.50 (br, 20H), 3.37 (s, 6H). $^{13}$C-NMR (300 MHz, CDCl$_3$, 25 °C) δ 149.61, 105.13, 73.48, 71.93, 71.07, 70.48, 70.33, 70.02, 58.99, 47.71. HR-MS (ESI) m/z calculated for C$_{19}$H$_{33}$O$_8$S [m+1] 421.19, found 421.1891.
Figure A. 1 – $^1$H-NMR spectrum of compound (2) in CDCl$_3$. 
Figure A. 2 – $^{13}$C-NMR spectrum of compound (2) in CDCl$_3$. 
Scheme A. 2 – Polymerization toward polymer G2-DMP.

![Scheme A. 2](image)

Compound (2) (0.1454 g, 1.0 equiv.), compound (3) (0.1182 g, 1.0 equiv.), pivalic acid (PivOH, 0.011 g, 0.30 equiv.), potassium carbonate (K$_2$CO$_3$, 0.1433 g, 3.0 equiv.), and a stir bar were added to a flame-dried and evacuated 15 mL Schlenk flask at room temperature. The reagents were then dissolved by addition of anhydrous DMAc (3.5 mL). Following addition, the flask was sealed and allowed to stir while concurrently purging with argon for 10 min. Finally, palladium (II) acetate (0.0016 g, 2 mol %), was added to the reaction mixture, which was then heated to 140 °C and allowed to stir for 12 h under positive argon pressure. After the flask was removed from heat and allowed to cool to 50 °C, the reaction vessel was charged with ~30 mg of diethylammonium diethyldithiocarbamate (palladium scavenger) and stirred for an additional 2 h. The polymer was then precipitated into methanol and filtered into a soxhlet extraction thimble. Washes were performed using methanol, acetone, hexanes, and DCM before finally dissolving the polymer into chloroform (CHCl$_3$). After dissolution, the CHCl$_3$ was removed under reduced pressure via rotary evaporation until ~2 mL of polymer solution
remained. The polymer was then precipitated in methanol and dried under high vacuum overnight. The product was obtained as a purple, flaky solid in 78 % yield (0.52 g). $^1$H-NMR (400 MHz, CDCl$_3$, 50 °C) $\delta$ (ppm) 4.18 (s, 4H), 3.85 (s, 4H), 3.77-3.45 (m, 20H), 3.36 (s, 6H), 1.15 (s, 6H). Anal. calcd. for C$_{28}$H$_{40}$O$_{10}$S$_2$: C, 55.98; H, 6.71; S, 10.67, Found: C, 55.22; H, 6.44; S, 10.48. Mn = 13.4 kDa, D = 1.6 vs. PS in CHCl$_3$ at 40 °C.

Figure A. 3 – $^1$H-NMR spectrum of polymer G2-DMP in CDCl$_3$. 

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Figure A. 4 – Gel permeation chromatogram of polymer G2-DMP in CHCl₃ at 40° C. 
$M_n = 13.4 \text{ kDa}, D = 1.6$ vs. PS.

A.1.1 Preparation of Polymer G4-DMP

A.1.1.1 Synthesis of Compound (4)

Scheme A. 3 – Synthesis towards compound (4).
Sodium hydride (NaH, 0.631 g, 26.31 mmol, 3 equiv.) and a stir bar were added to a flame-dried 250 mL round bottom flask under inert atmosphere. Compound (1) (3.00 g, 8.77 mmol, 1 equiv.) and 100 mL of anhydrous DMAc were mixed separately and added to the flame-dried 250 mL round bottom flask via cannulation. The resulting mixture of NaH, compound (1), and DMAc was purged with argon while stirring at room temperature for 30 min. Tetraethylene glycol monomethyl ether (5.48 g, 26.31 mmol, 3 equiv.) was then added dropwise to the reaction mixture while stirring. After addition, the reaction mixture was heated to 120 °C and allowed to stir vigorously for 16 h under positive argon pressure. Once the reaction was complete, the mixture was cooled to ambient temperature, extracted with DCM, and washed with deionized water. The organic layer was then washed repeatedly with brine. The organic phase was collected and subsequently concentrated under reduced pressure via rotary evaporation and purified by column chromatography using an EtOAc/hexanes (4:1) mobile phase. The product was obtained as a highly viscous, clear oil with a faint yellow hue in a 49% yield (2.58 g). $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) $\delta$ (ppm) 6.44 (s, 2H), 4.01 (s, 4H), 3.70-3.50 (br, 36H), 3.37 (s, 6H). $^{13}$C-NMR $\delta$ 149.68, 105.19, 73.56, 71.94, 71.12, 70.65, 70.62, 70.59, 70.53, 70.36, 70.11, 59.05, 47.77. HR-MS (ESI) m/z calculated for C$_{27}$H$_{49}$O$_{12}$S [m+1] 597.29, found 597.2939.
Figure A. 5 – $^1$H-NMR spectrum of compound (4) in CDCl$_3$. 
Figure A. 6 – $^{13}$C-NMR spectrum of compound (4) in CDCl$_3$.

A.1.1.1 Synthesis of Polymer G4-DMP

Scheme A. 4 – Polymerization toward polymer G4-DMP.
Compound (4) (0.2156 g, 1.0 equiv.), compound (3) (0.1450 g, 1.0 equiv.), pivalic acid (PivOH, 0.013 g, 0.30 equiv.), potassium carbonate (0.1758 g, 3.0 equiv.), and a stir bar were added to a flame-dried and evacuated 15 mL Schlenk flask at room temperature. The reagents were then dissolved by addition of anhydrous DMAc (4.2 mL). Following addition, the flask was sealed and allowed to stir while concurrently purging with argon for 10 min. Then, palladium (II) acetate (0.0019 g, 2 mol %), was added to the reaction mixture, which was then heated to 140 °C and allowed to stir for 12 h under positive argon pressure. After the flask was removed from heat and allowed to cool to 50 °C, the reaction vessel was charged with ~30 mg of diethylammonium diethyldithiocarbamate (palladium scavenger) and stirred for an additional 2 h. The polymer was then precipitated into methanol and filtered into a soxhlet extraction thimble. Washes were performed using methanol, acetone, hexanes, and tetrahydrofuran before finally dissolving the polymer into chloroform. After dissolution, the chloroform was removed under reduced pressure via rotary evaporation until ~2 mL of polymer solution remained. The polymer was then precipitated in methanol and dried under high vacuum overnight. The product was obtained as a shiny purple, fibrous solid in 86 % yield (0.29 g). $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ (ppm) 4.19 (s, 4H), 3.85 (s, 4H), 3.77-3.45 (m, 36H), 3.35 (s, 6H), 1.15 (s, 6H). Anal. calcd. for C$_{36}$H$_{56}$O$_{14}$S$_2$: C, 55.65; H, 7.27; S, 8.24, Found: C, 55.38; H, 7.04; S, 8.53. $M_n$ = 65.9 kDa, $D$ = 2.5 vs. PS in CHCl$_3$ at 40 °C.
Figure A. 7 – $^1$H-NMR spectrum of polymer G4-DMP in CDCl$_3$. 
Figure A. 8 – Gel permeation chromatogram of polymer G4-DMP in CHCl₃ at 40° C. 
$M_n = 65.9$ kDa, $D = 2.5$ vs. PS.
A.1 Synthesis and Structural Characterization of Polymer G3-DEHP

Polymer G3-DEHP (reported in CHAPTER 6) and associated monomer precursors were prepared by Brandon T. DiTullio (GT). The synthetic procedures and structural characterization of this material is provided herein.

A.1.1 Materials and Methods

All reagents were purchased and used as received from commercial suppliers: Pd(OAc)2 (99.9%, Acros Organics), pivalic acid (99%, TCI America), K₂CO₃ (anhydrous, VWR), triethylene glycol monomethyl ether (98%, TCI America), N-bromosuccinimide (99% NBS, Sigma Aldrich), NaH (90%, Sigma Aldrich), and diethylthiocarbamic acid diethylammonium salt (97%, TCI America). Dimethylacetamide (HPLC grade DMAc, VWR) was degassed by argon bubbling and stored over molecular sieves prior to use. Gel permeation chromatography (GPC) was performed using a Tosoh EcoSEC GPC equipped with an RI detector to determine the number average molecular weight (Mₙ), weight average molecular weight (Mₙw), and dispersity (Đ) relative to polystyrene (PS) standards. Chloroform (40 °C, HPLC grade) was used as the GPC eluent. Silica used for purification by column chromatography (60 Å porosity) was purchased from Sorbent Technologies, Inc. NMR spectroscopy for all monomers, precursors, and reagents was conducted using a Varian Mercury Vx 300 MHz instrument with CDCl₃ as the solvent. The residual CHCl₃ peak was used as a reference for all reported monomer chemical shifts (¹H: δ= 7.26 ppm, ¹³C: δ= 77.16 ppm). ¹H-NMR spectroscopy of Polymer G3-DEHP was performed using a Bruker AVIII-400 MHz instrument with C₂D₂Cl₄ as the solvent at 100 °C. Elemental analysis was completed by Atlantic Microlab Inc.
Compound (5) (ProDOT(G3)_3)^{227} and compound (6) (ProDOT(DEH)-Br)_2^{6,132} were prepared and purified according to previous reports and characterized using ^1H-NMR, ^13C-NMR, and GC-MS analysis.

A.1.1 Synthesis of Polymer G3-DEHP

Scheme A. 5 – Polymerization towards polymer G3-DEHP.

Compound (5) (0.3565 g, 1.0 equiv), compound (6) (0.4189 g, 1.0 equiv), pivalic acid (0.025 g, 0.3 equiv), potassium carbonate (0.242 g, 2.5 equiv), and a stir bar were added to a flame-dried and evacuated 15 mL Schlenk flask at room temperature. The reagents were then dissolved by addition of anhydrous N,N-dimethylacetamide (4 mL). Following addition, the flask was sealed and allowed to stir while concurrently purging with argon for 10 min. Finally, the catalyst, palladium (II) acetate (0.003 g, 2 mol %), was added to the reaction mixture, which was then heated to 140 °C and allowed to stir for 12 hours under argon pressure. After the flask was removed from heat and allowed to cool to 50 °C, the reaction vessel was charged with ~30 mg of diethylammonium diethylidithiocarbamate (palladium scavenger) and stirred for two additional hours. The polymer was then precipitated into methanol and filtered into a soxhlet extraction thimble.
Washes were performed using methanol, acetone, and hexanes, before finally dissolving the polymer into chloroform. After dissolution, the chloroform was removed until ~2 mL of polymer solution remained. The polymer was then precipitated in methanol and dried under high vacuum overnight. The product was obtained as a purple solid in 78 % yield (0.52 g). \textsuperscript{1}H-NMR (400 MHz, C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4}, 100 °C) \(\delta\) (ppm) 4.23 (s, 8H), 3.78-3.41 (m, 36H), 3.39 (s, 6H), 1.61 (m, 2H), 1.39 (m, 16H), 0.98 (m, 12H). Anal. calcd. for C\textsubscript{48}H\textsubscript{82}O\textsubscript{14}S\textsubscript{2}: C, 60.86; H, 8.73; S, 6.77, Found: C, 61.16; H, 8.58; S, 6.62. \(M_n = 23.8\) kDa, \(\mathcal{D} = 1.5\) vs. PS in CHCl\textsubscript{3} at 40 °C.

Figure A. 9 – \textsuperscript{1}H-NMR spectrum of polymer G3-DEHP in C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4} (100 °C).
Figure A. 10 – Gel permeation chromatogram of polymer G3-DEHP in CHCl$_3$ at 40° C. $M_n = 23.8$ kDa, $D = 1.5$ vs. PS.
REFERENCES


(57) Heinze, J.; Frontana-Uribe, B. A.; Ludwigs, S. Electrochemistry of Conducting


Kerszulis, J. A. Reading the Rainbow: Tailoring the Properties of Electrochromic Polymers, Georgia Institute of Technology, 2014.


(111) Sun, H.; Vagin, M.; Wang, S.; Crispin, X.; Forchheimer, R.; Berggren, M.; Fabiano, S. Complementary Logic Circuits Based on High-Performance n-Type Organic


(114) Pyo, M.; Reynolds, J. R. Electrochemically Stimulated Adenosine 5′-Triphosphate (ATP) Release through Redox Switching of Conducting Polypyrrole Films and Bilayers.


(123) Dyer, A. L.; Thompson, E. J.; Reynolds, J. R. Completing the Color Palette with


(134) Kerszulis, J. A.; Amb, C. M.; Dyer, A. L.; Reynolds, J. R. Follow the Yellow Brick


(142) Thackeray, J. W.; Wrighton, M. S. Chemically Responsive Microelectrochemical Devices Based on Platinized Poly(3-Methylthiophene): Variation in Conductivity

417


(156) Feig, V. R.; Tran, H.; Lee, M.; Bao, Z. Mechanically Tunable Conductive


(168) Gentili, D.; D’Angelo, P.; Militano, F.; Mazzei, R.; Poerio, T.; Brucale, M.;


(177) Khodagholy, D.; Gelinas, J. N.; Zhao, Z.; Yeh, M.; Long, M.; Greenlee, J. D.; Doyle, W.; Devinsky, O.; Buzsáki, G. Organic Electronics for High-Resolution


421


(239) Wolfe, R. M. W. THE IMPACT AND ROLE OF SYNTHETIC CHEMISTRY IN
MATERIALS SCIENCE THE IMPACT AND ROLE OF SYNTHETIC CHEMISTRY IN, Georgia Institute of Technology, 2018.


(365) Georgia Tech Brand Standards https://brand.gatech.edu/brand/colors.


(411) Harris, J. K.; Neelamraju, B.; Ratcliff, E. L. Intersystem Subpopulation Charge


Made from Conducting Nanowire Networks Self-Assembled from Amyloid Fibrils and Alkoxy sulfonate PEDOT. *Nano Lett.* **2008**, *8* (6), 1736–1740.


(441) Zhang, M.; Zhou, Q.; Chen, J.; Yu, X.; Huang, L.; Li, Y.; Li, C.; Shi, G. An Ultrahigh-Rate Electrochemical Capacitor Based on Solution-Processed Highly


Matta, M.; Wu, R.; Paulsen, B. D.; Petty, A. J.; Sheelamanthula, R.; McCulloch, I.; Schatz, G. C.; Rivnay, J. Ion Coordination and Chelation in a Glycolated Polymer


