Installation of a reactive site for covalent wiring onto an intrinsically conductive poly(ionic liquid)

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Abstract

Post-polymerization radical bromination of a nanostructured poly(ionic liquid) that selectively introduces a reactive bromo-group onto the polyalkylthiophene backbone is described. Raman and FT-IR spectroscopy proves that the bromine is successfully introduced at the 3-methyl position of the thiophene and that the molecular structure of the polymer remains largely intact with only minimal chain scission detected. FT-IR and Vis-NIR spectroscopy indicates that incorporation of the bromine induces twisting (loss of co-planarity) of the polythiophene backbone. WAXS confirms retention of an ordered lamellar structure with minor lattice spacing contraction. Cyclic voltammetry confirms spectroscopic findings that the bromination reaction yields a stable *p*-doped polymer. The installed bromine is susceptible to nucleophilic displacement permitting the covalent attachment of other functional molecules, such as a dialkylphosphonate. Elemental analysis of such a transformation established that 100 % functionalization can be achieved. These results collectively demonstrate that post-modification of a π -conjugated polymer can be used to both tune electronic and photonic properties, as well as install a chemoselective attachment point for the covalent wiring of other molecules.

Keywords: Functional interfaces, post-polymerization radical bromination, poly(ionic liquid), dual conductive polymers.

1. Introduction

There is ongoing need for materials and approaches for “wiring” biological components to traditional electronic materials. Bioelectronic interfacial materials that are both ion and electron conducting, mechanically compliant, operable within a biological environment (water) and possess unique functional moieties for the chemoselective coupling (“wiring”) of electro-active components are important for advancing neuroprosthetics and bio-hybrid energy converting systems.¹⁻⁵ Conducting polyelectrolytes, possessing dual electronic and ionic charge transport, may be an ideal platform for the development of interfacial materials optimized for signal transduction between traditional inorganic conductors and biological systems. To date, the majority of research exploring the coupling of proteins to conducting polymeric materials has been directed at physical adsorption (entrapment) of the protein to a conducting polymer.^{4,6,7} While this approach benefits from simplicity, it often suffers from loss of the active biological component to its surroundings (diffusion), inefficient communication between coupled entities, and the inability to construct hierarchical structures which perform a cascade of reactions or events. Recently, plasma immersion ion implantation was used to carry out linker-free covalent functionalization of polypyrrole to non-specifically bound cell adhesive proteins.⁸ A conductive polyelectrolyte containing a wiring element for covalent attachment would offer greater positional placement / organization of the functional components and stable, direct electronic communication. Post-polymerization modification offers a simple strategy for the creation of a functional interfaces, allowing the introduction of a unique functional group that may otherwise not be compatible with polymerization chemistry.⁹ Several post-functionalization strategies have been reported for both conducting¹⁰⁻¹⁵ and non-conducting polymers.^{16,17} For example, a wide range of reactive groups, including carboxylic acids^{10,13,14}, amides¹⁴, amines¹⁰, thiols^{10,12,15} and halides¹²⁻¹⁵ have been introduced on polythiophene. Approaches applicable to the coupling of conductive systems to biomolecules include the activation of carbon nanotube surface hydroxyls or amines with 1,4-carbonyldiimidazole followed by reaction with amine-containing glucose oxidase.¹⁸ Alternatively, phage display identified polypyrrole specific peptides modified with biotin permitted binding to a streptavidin labeled molecule.¹⁹ Significant opportunities remain, however, for further developing intrinsically conducting polymers that enable site-specific, chemoselective ligation to biomolecules.

Exploitation of unique naturally occurring amino acids such as cysteine offer a route to achieving selective coupling to a protein.²⁰ For example, cysteines can form disulfide bonds with sulfhydryl functionalized materials. However, disulfide bonds are prone to reduction, hence their stability is poor. Alternatively, thioethers formed by the coupling of a haloalkane to a cysteine

provide a more robust coupling strategy.²¹ Given that both imidazolium-based poly(ionic liquids)^{4,22,23} and functionalized polythiophenes²⁴⁻²⁶ have independently proven to be biocompatible with a range of proteins, the introduction of a haloalkane functional group on an intrinsically conductive polyelectrolyte may offer a simple means for developing a protein compatible interfacial conductor for the electrical wiring of biomolecules.

Previously, we reported ionic liquid monomers, containing either a thienyl or a propargyl moiety that could be either chemically or electro-polymerized to form π -conjugated polyelectrolytes.²⁷⁻²⁹ More specifically, one of these constructs were formed from a bifunctional monomer containing a thienyl group on the terminus of a C₁₀ alkyl chain and a vinyl moiety appended to the imidazolium headgroup polymerized to form a well-ordered film that exhibited good electronic transport.²⁷ The as-synthesized polymer lacked a necessary functional group for the covalent attachment of other molecules. The omission of such a reactive group was deliberate to facilitate the synthesis of the monomer and polymerization. In this report, we describe a facile post-polymerization modification that selectively introduces a bromo-group capable of undergoing nucleophilic displacement. The reactivity of the bromo-moiety is demonstrated by carrying out a simple nucleophilic displacement reaction, incorporation of a dialkylphosphonate. The work represents an important first step towards chemically tailoring a π -conjugated polyelectrolyte to promote direct electronic communication with appended electroactive biomolecules.

2. Materials and methods

2.1 Materials

Deuterated chloroform, *N*-bromosuccinimide (NBS), benzoyl peroxide, ammonium persulfate, ethanol, and carbon tetrachloride were purchased from Fisher Scientific (Pittsburgh, PA). Acetone was purchased from EMS Chemicals (Darmstadt, Germany). Ferric chloride, triethyl phosphite, and hydrazine were purchased from Sigma-Aldrich (St. Louis, MO). All reagents were used as received. Nanopure water (18 M Ω) was provided by a Milli-Q water purification system.

2.2 Synthesis

Poly(1-(10-((4-(bromomethyl)thiophen-3-yl)oxy)decyl)-3-vinylimidazolium bromide), poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] (**2**). Bromination of poly(1-(10-((4-methylthiophen-3-yl)oxy)decyl)-3-vinylimidazolium bromide), poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] (**1**) was carried out using radical bromination on either the bulk, thermal free radical prepared polymer or the thin film,

electropolymerized on ITO coated glass. The representative synthetic procedure carried out on a segment of the solid bulk is as follows. In a 25 mL round bottom flask equipped with a stir bar, 85 mg of the solid polymer (**1**) (0.20 mmol, 1.0 eq.), 35 mg of *N*-bromosuccinimide (0.20 mmol, 1.0 eq.) and 0.5 mg of benzoyl peroxide (0.002 mmol, 0.01 eq.) were introduced. Carbon tetrachloride (3 mL) was added to the flask and the mixture was allowed to stir overnight at room temperature and in the absence of ambient lighting, facilitating infiltration of the reactants. After stirring overnight, an additional 35 mg of *N*-bromosuccinimide (0.20 mmol, 1.0 eq.) and 0.5 mg of benzoyl peroxide (0.002 mmol, 0.01 eq.) were added. The flask was equipped with a condenser and the mixture was heated to reflux for 5 h. The dark brown solid polymer was recovered by filtration, rinsed with acetone and then Soxhlet extracted with acetone overnight to remove residual *N*-bromosuccinimide and the succinimide byproduct. The resulting brown solid was oven dried at 85 °C for 3 h. 66 mg of poly(1-(10-((4-(bromomethyl)thiophen-3-yl)oxy)decyl)-3-vinylimidazolium bromide) (**2**) was recovered. ATR/FT-IR (cm⁻¹): 3397, 3254, 2927, 2854, 1713, 1568, 1497, 1462, 1363, 1224, 1167, 1114, 1023, 968, 877, 830, 754, 723, 654.

Poly(1-(10-((4-((diethoxyphosphoryl)methyl)thiophen-3-yl)oxy)decyl)-3-vinylimidazolium bromide), poly[3-VImC₁₀O-4-MPhosThienyl⁺][Br⁻] (**3**). The phosphonate group was introduced by suspending 10 mg (0.020 mmol) of the solid bromomethyl-functionalized polymer (**2**) in 20 mL of triethyl phosphite. The mixture was brought to reflux and allowed to react overnight. After cooling, the solids were filtered out and washed with copious amounts of ethanol. The recovered solid was dried in a Kugelrohr setup at 100 °C and 20 mTorr for 3 h. ATR/FT-IR (cm⁻¹): 3422, 3236, 3137, 2927, 2851, 1714, 1641, 1568, 1464, 1370, 1254, 1169, 1058, 982, 943, 900, 879, 853, 770, 720, 692, 657, 624, 601. Elemental Analysis calculated for C₂₄H₃₈N₂O₄PSBr (561.5123 g/mol): P, 5.52; S, 5.71; Found: P, 5.64; S, 5.77.

De-doped poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻]. De-doped (**2**) was obtained by treating the as-synthesized polymer (15 mg, 0.030 mmol) with 3 mL solution of 17.5% (w/v) hydrazine in 1:1 ethanol:water. The solution was gently stirred overnight. The solids were then filtered out and rinsed with copious amounts of ethanol. The material was allowed to dry under a flow of argon gas. The recovered solid was orange-brown. ATR/FT-IR (cm⁻¹): 3397, 3343, 3136, 2929, 2859, 1709, 1670, 1606, 1568, 1462, 1364, 1312, 1239, 1166, 1092, 1049, 1024, 970, 879, 757, 723, 693, 654, 620, 602.

P-doping poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻]. Oxidation and re-doping was accomplished by suspending 15 mg (0.030 mmol) of **3** in 2 mL of an 11 mg/mL solution of ferric chloride in water. The mixture was gently stirred for 3 h. Two mL of a 13 mg/mL solution of ammonium persulfate in water were then added and the mixture was allowed to stir overnight. The solids were filtered out and rinsed with copious amounts of water. The material was allowed to dry under a flow of argon gas. A brown solid was recovered. ATR/FT-IR (cm⁻¹): 3413, 3255, 3147, 2929, 2853, 1766, 1709, 1671, 1565, 1462, 1379, 1364, 1340, 1209, 1163, 1046, 1024, 971, 879, 850, 755, 724, 693, 660, 617.

Bromine-doped poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻]. Poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] (**1**, 10 mg, 0.024 mmol) was placed in a small uncapped vial and placed inside the larger vial containing 1 drop of elemental bromine and capped. The bromine vapors were allowed to diffuse into the polymer for 1 h. The brownish sample was removed and placed in a flask and flushed briefly with Ar and taken for IR spectroscopy. The bromine gas treated sample was Soxhlet extracted with acetone for 5 hours and then analyzed by IR spectroscopy. ATR/FT-IR (cm⁻¹) bromine exposed: 3145, 2933, 2858, 1700, 1678, 1570, 1547, 1510, 1464, 1427, 1407, 1383, 1357, 1278, 1220, 1157, 1107, 1055, 964, 920, 877, 746, 665, 651, 623. ATR/FT-IR (cm⁻¹) Soxhlet extracted: 3363, 3297, 3114, 2930, 2856, 1678, 1639, 1570, 1550, 1527, 1510, 1465, 1438, 1411, 1380, 1365, 1315, 1213, 1164, 1113, 1062, 885, 752, 721, 710, 683, 658, 621.

2.3 Physical Methods

ATR-FT-IR spectroscopy was performed using a Bruker Vertex 70 spectrometer. Data was collected from 4000-600 cm⁻¹ with a resolution of 4 cm⁻¹ and averaged over 256 scans. Raman spectra were obtained via a Renishaw inVia Raman microscopy (Renishaw Inc., Hoffman Estates, IL) employing a 785 nm laser beam and a CCD detector with 2.9 cm⁻¹ resolution. Each spectrum was recorded by using a 50-x objective and accumulated for ten times. Electrochemical characterization was performed using a BAS-EC Epsilon potentiostat (West Lafayette, IN) with a three-electrode configuration containing 0.1 M Bu₄NPF₆ in dichloromethane. A platinum wire and Ag/Ag⁺ electrode (0.1 M AgNO₃ in acetonitrile) were used as auxiliary and reference electrode, respectively. All reported potentials were given vs. Ag/Ag⁺. WAXS was performed at the Advanced Photon Source (APS) at Argonne National Laboratory on undulator beamline 12ID-B according to experimental procedures previously described.²⁷

d.c. conductivity measurement. The standard spring-loaded, pressure-contact, four probe method was employed for d.c. conductivity studies. A constant current (I_m) was passed from the probe (S-302-4, Lucas Labs, Gilroy, CA) to two diagonal leads, and the voltage (V_m) across the other two leads was measured using a Keithley model 2420 multimeter (Keithley Instruments, Cleveland, OH). The conductivity, σ (S/cm) was calculated using the following equation:

$$\sigma = [4.53 \times (V_m / I_m) \times d]^{-1}$$

where, d is the film thickness, measured using the Ambios XP-1 Stylus Profiler (Santa Cruz, CA) to be $3 \pm 0.5 \mu\text{m}$.

3. Results and Discussion

Electronically conductive poly(ionic liquid)s were synthesized as previously described from bifunctional imidazolium-based ionic liquids that incorporated both a vinyl group and a thiophene moiety, [3-VImC₁₀O-4-MThienyl⁺][Br⁻], (**1**)^{27,28} and [3-VImC₁₀O-4-MThienyl⁺][BF₄⁻].³⁰ Prior work showed that the nature of the counter-anion (i.e., bromide vs. tetrafluoroborate) is important for regulating whether the polymerization of the thienyl and vinyl moieties occurs simultaneously or sequentially.³⁰ The observed differences in reactivity between the bromide and tetrafluoroborate IL monomers were attributed to changes in the anion induced changes in ion pairing with the imidazolium-based cation.³⁰ While the two-step polymerization of the tetrafluoroborate monomer affords processability, the product material suffers from a reduction in electronic conductivity.³⁰ Single-step electropolymerization of the bromide monomer, while producing an insoluble (non-processable) material, was found to be a well-ordered polymer with good electronic conductivity.²⁷ Herein, we describe a facile means to introduce a unique reactive halogen into the polyalkylthiophene backbone of the insoluble electropolymerized [3-VImC₁₀O-4-MThienyl⁺][Br⁻] as a means to covalently couple or “wire” molecules to the electronically conductive core.

Installation of a bromine at the 3-methyl position on the thiophene ring was performed using Wohl-Ziegler radical conditions (Scheme 1).³¹ Briefly, a suspension of the solid polymer (**1**), *N*-bromosuccinimide and benzoyl peroxide in carbon tetrachloride was stirred at room temperature overnight. Carbon tetrachloride was used as the solvent since it allowed for both sufficient swelling of the polymer²⁸ and solubility of the reactants to promote infiltration throughout the interior of the solid polymer. Once the reactants were infiltrated into the solid polymer the mixture was refluxed for 5 h to afford the bromo-functionalized polymer, poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] (**2**). Post reaction, the solid polymer was exhaustively Soxhlet extracted with

acetone to remove unreacted *N*-bromosuccinimide and the corresponding succinimide byproduct. While the unreacted poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] is pale yellow, the brominated material is red-brown (Figure 1A). NMR spectroscopy of the bromo-functionalized (crosslinked) network polymer was not possible due to its lack of solubility in any solvent. Therefore, successful bromination of the methyl group on the thiophene ring was determined by vibrational spectroscopy and elemental analysis.

The Raman spectra collected on the parent poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] (black curve) and bromo-functionalized polymer, poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] (red curve) are compared in Figure 1B. A new mode at 625 cm⁻¹ emerges post-bromination, which is assigned to the C-Br stretching vibration.³² The FT-IR spectrum recorded on the bromo-functionalized polymer (Figure 2A, red curve) displays two modes (754 cm⁻¹ and 968 cm⁻¹) assigned to coupled CH₂Br and CH deformations that are not observed in the parent polymer (poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻]) (Figure 2A, black curve), providing additional confirmation that the bromine was successfully installed at the 3-methyl position.³³

Scheme 1. Synthesis and doping and de-doping reactions of poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻]

The extent of bromination was determined indirectly by converting it to the dialkylphosphonate and determining the phosphorous content by elemental analysis. Direct measurement of the bromine content cannot be made since the polymer possesses an exchangeable bromide counterion. The classic Michaelis-Arbuzov reaction was employed to

transform the installed bromine to the corresponding dialkylphosphonate since it is known in the literature to have very high conversion rates (Scheme 2).^{34,35} Removal of residual triethyl phosphite was accomplished by exhaustive washing with ethanol followed by heating to 100 °C under a high vacuum. Successful phosphonation of the polymer was confirmed by inspection of the FT-IR spectrum (Figure 2C) which lacked the two modes assigned to the coupled bromoalkane (754 cm⁻¹ and 968 cm⁻¹) with concomitant appearance of modes at 1254 cm⁻¹ ($\nu(\text{P}=\text{O})$) and 1058 cm⁻¹ ($\nu(\text{P}-\text{O}-\text{C})$).³⁶ A relative molar ratio of phosphorus (from phosphonate) to sulfur (from thienyl) was determined to be a 1:1 by elemental analysis, providing indirect evidence that the methyl groups on the polymer thienyl rings were completely (100%) functionalized with bromine. High conversion to the dialkylphosphonate also demonstrates sufficient accessibility and reactivity of the appended bromine.

Scheme 2. Synthesis of poly[3-VImC₁₀O-4-MPhosThienyl⁺][Br⁻]

Insights into the redox state of the polythiophene post-bromination can also be gleaned from evaluation of its vibrational spectrum. As shown in Figure 2B, the C=C thienyl stretching mode undergoes a shift to higher wavenumber (from 1671 cm⁻¹ to 1713 cm⁻¹). Previously, it had been noted that the force constant can increase with increasing quinoidal character of the polythiophene chain, shifting the IR band to higher wavenumbers.³⁷ This type of arrangement is present in the bipolaronic structure of *p*-doped polythiophene (Scheme 1, *p*-doped **2**). The enhanced quinoid geometry (increased double bond character of the thiophene inter-ring) upon *p*-doping has been observed for polymerized poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] which had been chemically oxidized with FeCl₃.²⁸ In addition, the appearance of a mode at 1224 cm⁻¹ and the disappearance of a mode at 1310 cm⁻¹ are also indicators of a *p*-doped state.³⁸ It is possible that *p*-doping occurs from a low concentration of Br₂ generated during the radical bromination process.

The bromo-functionalized *p*-doped polymer was de-doped by treatment with an aqueous, ethanolic solution of hydrazine. The IR collected on the de-doped polymer is shown in Figure 3A, green curve. The diagnostic *p*-doping mode at 1713 cm⁻¹ shifts to 1709 cm⁻¹ and is

significantly diminished in amplitude while the mode at 1670 cm^{-1} is intensified. Additional confirmation of the formation of a de-doped bromo-functionalized polymer is indicated by the appearance of modes at 1606 , 1239 , and 1092 cm^{-1} . The freshly de-doped polymer was then chemically re-oxidized, employing an aqueous solution of FeCl_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to re-generate the *p*-doped bromo-functionalized polymer (Figure 3A, orange curve). Post treatment, significant strengthening of the 1709 cm^{-1} mode and concomitant weakening of the 1670 cm^{-1} mode is observed. Complete loss of the 1606 and 1092 cm^{-1} modes, consistent with formation of the *p*-doped bromo-functionalized polymer is observed. It is noted, however, that complete conversion to the de-doped (neutral) and *p*-doped states by chemical reduction and oxidation were not achieved. The incomplete transformation between redox states is attributed to poor permeation of the aqueous solution of reductant and / or oxidant through the interior core of the polymer.²⁸

The as-synthesized *p*-doped bromo-functionalized polymer did display good stability with extended storage under ambient laboratory conditions. The enhanced stability of the polymer is illustrated by comparison of the FT-IR spectrum recorded on the freshly prepared bromo-functionalized polymer to one after 6 months of storage (Figure 3B). This stability is in stark contrast to that observed for the chemically *p*-doped non-brominated polymer which reverts to the neutral state within hours under ambient conditions.²⁸

As a test of the importance of the electron withdrawing bromine leading to retention of the *p*-doped state, the effect of exposure of Br_2 vapor to the non-brominated, parent poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] was examined (Figure 3C). Immediately after exposure to Br_2 vapor, the collected FT-IR spectrum on the product (Figure 3C, orange curve) shows strong modes at 1700 cm^{-1} and 1278 cm^{-1} characteristic of the formation of the *p*-doped poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻]. After Soxhlet extraction with acetone, the Br_2 treated poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] FT-IR spectrum shows the loss of the 1700 cm^{-1} and 1278 cm^{-1} modes, and the re-appearance of the 1678 cm^{-1} mode, indicating complete loss of the dopant and conversion back to the neutral, de-doped polymer (Figure 3C, blue curve). The facile conversion back to the neutral form of the polymer arises from the loss of the volatile Br_2 dopant and is in contrast to the *p*-doped brominated polymer which resists de-doping even during Soxhlet extraction with acetone and long term storage under ambient conditions. Thus, while generation of Br_2 during the bromination may facilitate the formation of a *p*-doped polymer, the introduction of the bromine group on to the thienyl ring aids in stabilizing the oxidized form of the polymer.

In addition to the observed changes in the redox state of the polymer post-bromination, comparison of the IR spectra collected on parent poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] to poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] reveals some minor changes in the thienyl modes (Figure 2B).

Several new modes emerge, including two C-H “out-of-plane” deformations at 654 cm^{-1} and 830 cm^{-1} (weak), suggesting an increase in terminal thiophene ring content.³⁹ The increase in terminal thiophene rings implies a reduction in chain length possibly arising from chain scission as a result of bromination. Polymer oxidation has been known to lead to chain scission.⁴⁰ A reduction in thiophene backbone conjugation, which could also arise from backbone conformational changes, is also indicated by an increase in the intensity ratio between the symmetric (1462 cm^{-1}) and antisymmetric (1497 cm^{-1}) $\text{C}_\alpha=\text{C}_\beta$ thienylene stretches compared to the non-brominated polymer.⁴¹ The extent of chain scission is not believed to be too extensive considering that the gross mechanical properties (i.e., the polymer remains a self-supporting solid that does not undergo dissolution in common organic solvents) of the polymer have not been altered (Figure 1A).

The optical characteristics of the bromo-functionalized polymer were evaluated in the visible-NIR spectral range on an electrodeposited film (Figure 4). The electrochromic behavior of poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] has been previously reported where incremental changes in the applied potential revealed dramatic changes in the absorption spectrum.²⁷ Specifically, in the neutral state (0 V) the $\pi-\pi^*$ absorption band was observed at 380 nm. At intermediate applied potential (0.6 V), the absorption peak red-shifted to 672 nm and was accompanied by a reduction in the $\pi-\pi^*$ peak intensity, signaling the formation of polaronic charge carriers. Further oxidation (1.2 V) caused additional reduction in the $\pi-\pi^*$ band and further red-shifting of the absorption peak into the NIR region (> 800 nm). The spectrum recorded on the bromo-functionalized polymer displays both a $\pi-\pi^*$ transition at 368 nm and a very broad absorption at 500 nm which extends into the NIR (Figure 4). The center maximum of the absorption within the visible-NIR is at ca. 612 nm. The observed spectral features recorded on the brominated polymer compares well with that previously determined for the unfunctionalized polymer in the bipolaronic (metallic) state.²⁷ The optical spectrum confirms that bromination produces a stable *p*-doped polymer. The blue shifting in the absorption bands relative to those previously recorded for the unfunctionalized polymer implies a shortening of the effective conjugation length, leading to a reduction in the π -electron delocalization along the polythiophene backbone. Thus, both FT-IR and optical spectroscopy indicate that incorporation of the bromine on the thiophene ring causes some degree of twisting and loss of co-planarity. Such an observation is consistent with prior work on polythiophene derivatives demonstrating that appended bulky groups tend to reduce the effective conjugation length of the backbone.⁴²

Spectroscopic characterization of the brominated polymer also suggests changes in architecture. Thus, the film was interrogated using wide-angle X-ray scattering (WAXS). A

representative diffraction pattern collected on an electropolymerized bromo-functionalized polymer is presented in Figure 5A. The azimuthally averaged data shows six orders of lamellar diffraction positioned at $q = 0.061, 0.80, 1.02, 1.27, 1.49, 1.61 \text{ \AA}^{-1}$ which index to the (300), (400), (500), (600), (700), and (800) reflections (Figure 5B). A repeat distance of 3.1 nm is determined, a value ca. 1 Å less than that previously determined for the non-brominated polymer.²⁷ Noticeably absent in the wide-angle data are reflections associated with short-range ordering of the imidazolium cation and / or the π - π stacking of the thienyl moieties.²⁷ Collectively, the scattering data suggests that high density installation of the bromine (100% functionalization) causes perturbation (loss) of short-range structural ordering and a minor contraction in lattice spacing.

A representative CV collected on the electrodeposited bromo-functionalized polymer is presented in Figure 6. Compared to the non-brominated parent polymer²⁷, the CV recorded on the bromo-functionalized electrodeposited polymer (Figure 6) lacks a *p*-doping wave. As previously reported, the parent polymer showed an oxidation peak positioned at 1.66 V (vs. Ag/AgCl).²⁷ The absence of a *p*-doping oxidation peak in the bromo-functionalized polymer is consistent with the spectroscopic data indicating that the polymer becomes *p*-doped during bromination. A reduction peak occurs at -1.32 V (vs. Ag/AgCl) with a corresponding oxidation peak at -1.37 in the reverse scan. A large, irreversible cathodic wave centered at -2.03 V (vs. Ag/AgCl) is also observed. The parent, non-brominated, polymer also displays an irreversible cathodic wave (at 1.78 V vs. Ag/AgCl). Thus, bromination appears to render the polymer less susceptible to irreversible degradation. A similar observation has been reported for chloro-functionalized polythiophenes.⁴³ The electrochemical studies show that introduction of an electron-withdrawing bromine on the thiophene improves the *n*-dopability of the polymer.⁴⁴

The conductivity for the bromo-functionalized polymer was determined to be $0.28 \pm 0.096 \text{ S cm}^{-1}$, a value an order of magnitude smaller than that previously determined for the I₂-doped non-brominated polymer (2.36 S cm^{-1}).²⁷ Nonetheless, the conductivity for the bromo-functionalized polymer remains higher than many typical polyalkylthiophenes.^{45,46} The reduction in conductivity for the (*p*-doped) brominated polymer most likely arises from the reduced structural ordering and co-planarity of the polymerized thiophene backbone induced by insertion of the bromine on the thiophene ring. While insertion of the bromine causes changes in the backbone conformation, it does have the advantage of inducing a stable *p*-doped material. The persistent *p*-doping means that the polymer does not suffer from the well established environmental instabilities of many chemically doped polyalkylthiophenes.⁴⁷ It is possible that the conductivity could be further increased by improving structural ordering by lowering the

functionalization level of the appended bromines. Future experiments will examine the interplay between the degree of functionalization, structural ordering and electronic properties.

4. Conclusions

A chemically reactive bromine moiety is incorporated into an electronically conductive polymerized ionic liquid. Installation of the bromine at the 3-methyl position of the thiophene using Wohl-Ziegler radical conditions proceeded at 100% functionalization. The post-functionalized polymer retains its mechanical integrity, but vibrational spectroscopy indicates loss of polythiophene backbone planarity, and the occurrence of chain scission attributed to the bromination. The induced conformational changes in the polythiophene backbone were further confirmed by the blue shifting of the π - π^* transition in the Vis-NIR absorption spectrum. WAXS confirmed the retention of the lamellar structure similar to that of the previously reported electropolymerized non-brominated polymer. Additionally, a minor (1 Å) reduction in d -spacing was determined. The reduction in the lattice spacing and the absence of diffraction peaks associated with short range ordering arise from structural disorder (twisting) of the polythiophene backbone. The bromination reaction yields a p -doped bromo-functionalized polymer that resists de-doping (to a neutral thiophene) upon storage under ambient conditions. The enhanced stability of the p -doped polymer is in stark contrast to the chemically oxidized (p -doped) non-brominated polymer, which rapidly converts to the neutral state upon exposure to air. The electrical conductivity determined for the brominated polymer is slightly reduced compared to the non-brominated chemically oxidized polymer, but the value is considerably more stable upon exposure and long-term storage in air. The improved long-term stability of the p -doped polymer is an advantage which offsets the reduction in the magnitude of the conductivity.

Recent studies on polythiophene derivatives have reported that post-polymerization functionalization with side-chain sulfur-containing moieties, such as sulfinyl, can lead to improved chromic response and higher electrical conductivity, suggesting the physical properties are highly sensitive to the nature of the chemical constituent and number density.⁴⁸ Future studies will examine synthetic conditions generating an improvement in structure and hence conductivity. Specifically, means to reduce the number of appended bromine atoms to the polyalkylthiophene backbone will be explored. Lowering the degree of bromo-functionalization, achieved by reducing reaction time and / or adjustment of NBS stoichiometry, may also aid in reducing undesirable chain scission. The interplay between degree of functionalization, formation of a stable p -doped state and the polythiophene conformational structure will be studied. The work reported herein demonstrates a straightforward synthetic approach for the introduction of an electron withdrawing group that permits tuning of polymer electronic properties and installs a reactive group for the covalent wiring of other functional

molecules on a structured polyelectrolyte. Future studies will attempt to conjugate an electroactive protein via thioether bond formation to the poly(ionic liquid). It is anticipated that the bromo-functionalized polymer will serve as an attractive alternative biocompatible electrode for the construction of a biofuel cell.⁴ That is, rather than electrostatically adsorbing electrocatalytic enzymes (e.g., glucose oxidase) onto Au NP-poly(IL) composite electrodes⁴, the bromo-functionalized poly(IL) will allow for direct “wiring” of the enzyme, offering both improved protein stability and electron transfer rates. Evaluation of the electronic transport between the polymer and the appended enzyme will be examined in a future report. It is envisioned that the bromo-functionalized conductive poly(ionic liquid) will serve as an optimized interfacial material for the covalent wiring of a wide variety of electroactive biomolecules, serving to advance the field of bioelectronics.

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Figure Captions

- Figure 1.** (A) Photographs of poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻], left image and poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻], right image. (B) Raman spectra ($\lambda_{\text{ex}} = 785 \text{ nm}$) collected between 200 – 1,000 cm⁻¹ on poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻], black curve and poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻], red curve.
- Figure 2.** ATR/FT-IR collected on solid (A) poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻], as-synthesized (black curve) and poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] washed with acetone (red curve), in the spectral ranges 3600 – 800 cm⁻¹ (left panel) and 1000 – 650 cm⁻¹ (right panel). (B) poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] (red curve) and poly[3-VImC₁₀O-4-MPhosThienyl⁺][Br⁻] (purple curve) in the spectral ranges 3600 – 600 cm⁻¹ (left panel) and 1000 – 500 cm⁻¹ (right panel).
- Figure 3.** ATR/FT-IR collected on solid (A) as-synthesized poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] (red curve), de-doped poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] (green curve) and re-oxidized (p-doped) poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] (orange curve) (B) as-synthesized poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] (black curve) and poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] stored under ambient conditions for 6 months (red curve). (C) as-synthesized poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] (black curve), poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] exposure to Br₂ gas vapor (orange curve), poly[3-VImC₁₀O-4-MThienyl⁺][Br⁻] exposure to Br₂ vapor then Soxhlet extracted in acetone (blue curve).
- Figure 4.** Optical absorption spectrum recorded on as-synthesized electropolymerized poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻]
- Figure 5.** (A) WAXS pattern collected on an electrodeposited film of as-synthesized poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻]. (B) Schematic illustration of proposed structural ordering based upon X-ray scattering data.
- Figure 6.** Cyclic voltammogram (CV) of poly[3-VImC₁₀O-4-MBrThienyl⁺][Br⁻] film electrodeposited on an ITO electrode. CV collected in CH₂Cl₂ containing 0.1 M Bu₄NPF₆ at scan rate of 50 mV/s.

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Figure

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 6

TOC

chemoselective attachment points are installed on an intrinsically conductive polymerized ionic liquid for the covalent wiring of other functional molecules.