Electropolymerized Pyrrole Based Conductive Polymeric Ionic Liquids and their Application for Solid-Phase Microextraction

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Abstract
Pyrrole was covalently bonded to 1-methyl and 1-benzylimidazolium ionic liquids (ILs) via an N-substituted alkyl linkage to prepare electropolymerizable IL monomers with excellent thermal stability. The methylimidazolium IL, [pyrrole-C6MIm]+, was then electropolymerized on macro- and microelectrode materials to form conductive polymeric IL (CPIL)-modified surfaces. Electrochemical characterization of a 1.6 mm diameter Pt disk electrode modified with poly[pyrrole-C6MIm]+ demonstrated a selective uptake for an anionic redox probe while rejecting a cationic redox probe. Furthermore, electropolymerization of [pyrrole-C6MIm]+ doped with single-walled carbon nanotubes (SWNT) on 125 μm platinum wires produced 42 μm thick poly[pyrrole-C6MIm]+/SWNT films compared to 17 μm in the absence of SWNT and 5 μm for the previously reported poly[thiophene-C6MIm]+ coatings. The poly[pyrrole-C6MIm]+/SWNT films were prepared with reproducible thicknesses as well as thermal properties sufficient for high-temperature applications, such as solid-phase microextraction (SPME) with gas chromatographic analysis. The utilization of the CPIL sorbent materials in SPME experiments provided excellent extraction efficiencies and selectivity toward organic aromatic analytes. The CPIL sorbent coatings also yielded outstanding fiber-to-fiber reproducibility on the basis of extraction efficiencies and improved response for a range of analytes relative to commercial 100 μm poly(dimethylsiloxane) fibers when normalized for differences in film thickness. Poly[pyrrole-C6MIm]+ CPIL coatings doped with SWNT are therefore promising new sorbent materials for SPME analyses.

Keywords
conductive polymers, electroanalysis, electropolymerization, pyrrole-functionalized ionic liquids, solid-phase microextraction

Disciplines
Chemistry

Comments

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Supporting Information

ABSTRACT: Pyrrole was covalently bonded to 1-methyl and 1-benzylimidazolium ionic liquids (ILs) via an N-substituted alkyl linkage to prepare electropolymerizable IL monomers with excellent thermal stability. The methylimidazolium IL, [pyrrole-C₆MIm]⁺, was then electropolymerized on macro- and microelectrode materials to form conductive polymeric IL (CPIL)-modified surfaces. Electrochemical characterization of a 1.6 mm diameter Pt disk electrode modified with poly[pyrrole-C₆MIm]⁺ demonstrated a selective uptake for an anionic redox probe while rejecting a cationic redox probe. Furthermore, electropolymerization of [pyrrole-C₆MIm]⁺ doped with single-walled carbon nanotubes (SWNT) on 125 μm platinum wires produced 42 μm thick poly[pyrrole-C₆MIm]⁺/SWNT films compared to 17 μm in the absence of SWNT and 5 μm for the previously reported poly[thiophene-C₆MIm]⁺ coatings. The poly[pyrrole-C₆MIm]⁺/SWNT films were prepared with reproducible thicknesses as well as thermal properties sufficient for high-temperature applications, such as solid-phase microextraction (SPME) with gas chromatographic analysis. The utilization of the CPIL sorbent materials in SPME experiments provided excellent extraction efficiencies and selectivity toward organic aromatic analytes. The CPIL sorbent coatings also yielded outstanding fiber-to-fiber reproducibility on the basis of extraction efficiencies and improved response for a range of analytes relative to commercial 100 μm poly(dimethylsiloxane) fibers when normalized for differences in film thickness. Pol[ypyrrole-C₆MIm]⁺ CPIL coatings doped with SWNT are therefore promising new sorbent materials for SPME analyses.

KEYWORDS: electropolymerization, pyrrole-functionalized ionic liquids, conductive polymers, electroanalysis, solid-phase microextraction

1. INTRODUCTION

Electrochemical polymerization of organic heterocyclic monomers at controlled potentials has been one of the most amenable routes toward the fabrication of novel functional matrices on chemically modified electrode (CME) surfaces. In comparison to chemical polymerization, surface adhesion, spin coating, and solvent evaporation, electrochemical polymerization stands out for its excellent control over the deposition parameters and film quality. The process can produce uniform conducting organic thin films that strongly adhere to the support material with superior electrical contact. Organic heterocyclic monomers such as pyrrole, thiophene, aniline, and furan have all been explored and found to produce useful conductive coatings. To date, these coatings have been widely studied for many applications involving fuel cells, analytical sensing devices, and extraction matrices. Particularly relevant to this work, Pawliszyn and co-workers electropolymemrized pyrrole to create a polymeric sorbent coating for solid-phase microextraction (SPME) of a variety of compounds, including ionic analytes and volatile organic compounds.

Ionic liquids (ILs) are typically organic salts with melting points below 100 °C. In recent years, ILs have gained extensive attention as a class of “green” materials due to their attractive physicochemical characteristics, such as tunable viscosity, high thermal stability, nonflammability, low vapor pressure, and good ionic conductivity. Furthermore, the physicochemical properties of ILs are often manipulated by the choice of the cation and anion. As a result, ILs have been widely applied in materials science, electrochemistry, chromatography, organic synthesis, and sample preparation techniques like SPME.

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Application of ILs as thin coatings on different substrate materials is very challenging, as they tend to flow during use. Therefore, new immobilization techniques, such as chemical polymerization, have been explored to improve the robustness of IL coatings to fully take advantage of their physicochemical properties. In these studies, electropolymerization of the thiophene-based IL monomers yielded mechanically and thermally stable films with unique optical properties. From an analytical perspective, the ability to tune the physicochemical properties of the thin film via the IL moiety and reproducibly coat surfaces by electropolymerization is a very attractive way to prepare robust films and create highly selective devices for analysis. Recognizing the lack of exploration of conductive polymeric ILs (CPILs) for analytical applications, our groups demonstrated that imidazolium IL-functionalized thiophenes can be electrochemically polymerized onto different electrode geometries to prepare CMEs. CPIL-coated electrodes showed excellent selectivity by attracting anionic analytes and repelling cationic species for electroanalytical measurements. In addition, an effective and reproducible electrochemical coating approach was established to produce CPILs as sorbent coatings for SPME analysis. The CPIL-based sorbent coatings were prepared with a simple protocol with a high fiber-to-fiber reproducibility, an excellent thermal stability, and a high selectivity for polar analytes. However, one drawback for the thiophene-based CPILs as SPME sorbent coatings was the relatively thin films (5 μm) that resulted from electro-polymerization. A new approach to produce thicker and more versatile CPIL films for electroanalysis and SPME applications is described herein. An analogous series of CPIL pyrrole-based monomers were synthesized and electrochemically polymerized at a controlled potential to obtain novel polypyrrole-based CPILs. Furthermore, these pyrrole-based CPIL monomers were polymerized in the presence of single-walled carbon nanotubes (SWNT) on microelectrode substrates to fabricate sorbent coatings for SPME analyses. Compared with the previously reported thiophene-based CPILs, the pyrrole-based CPILs doped with SWNT showed dramatically greater film thicknesses, enhancing their utility in SPME applications.

2. EXPERIMENTAL METHODS

2.1. Materials. 1-Methylimidazolide (99%), 1-benzylimidazolide (99%), 1,6-dibromohexane (99%), pyrrole, acetonitrile, toluene, dichloromethane, N,N-dimethylformamide (DMF), ethyl acetate, sodium hydride, potassium ferricyanide ([K3Fe(CN)6]3−), cobalt(III) sepulchrate trichloride ([Co(Sep)Cl3], ammonium hexafluorophosphate ([NH4PF6]), TEMPO (2,2,6,6-tetramethyl-1-piperidinoloxyl-2, 2,6,6-tetramethylpiperidin-1-oxyl), ethyl benzene (99.8%), hexane (99%), heptane (99%), propyl butyrate (99%), m-xylene (99%), naphthalene (99%), acenaphthene (99%), phenanthrene (99%), fluoranthene (99%), and pyrene (99%) were purchased from Sigma-Aldrich (St. Louis, MO). Platinum wire (99.95%, 0.125 mm OD) was purchased from Goodfellow Cambridge, Ltd (Huntington, England). All materials except pyrrole, which was distilled before use, were used as received. All organic solvents were dried as needed before use. All aqueous solutions were prepared with deionized (DI) water (>18 Ω·cm).

2.2. Instrumentation. For compound characterization, an Avance III 600 MHz spectrometer (Bruker, Inc., Billerica, MA) was used to obtain NMR spectra. High-resolution mass spectrometry (HRMS) was performed using a Waters Synapt high-definition mass spectrometer with a nano-electrospray ionization (ESI) source (Waters, Milford, MA). Thermogravimetric analysis (TGA) was performed on a SDT-Q600 Simultaneous TGA–DTG instrument (TA Instruments, New Castle, DE). The morphology and thickness of the deposited films were evaluated with a JEOl JSM-7500F scanning electron microscope (JEOL USA, Inc., Peabody, MA). Fourier transform infrared (FTIR) spectroscopic measurements were obtained with a PerkinElmer Frontier spectrophotometer (Shelton, CT).

Electrochemistry was performed with an Epsilon-EC electroanalytical System (Bioanalytical Systems, Inc., West Lafayette, IN) in a three-electrode electrochemical cell. A modified or unmodified platinum electrode (Bioanalytical Systems, Inc., MF-2020) electrode, which was stored in 3 M NaCl. Deoxygenation was conducted by an argon purge before the electrochemical experiments.

For SPME experiments, SPME fiber holders and commercial poly(dimethylsiloxane) (PDMS) fibers (100 μm thickness) were obtained from Supelco (Belfonte, PA). Analysis was performed with an Agilent 7890B gas chromatograph (Agilent Technologies Inc., Santa Clara, CA) coupled to an Agilent 5977B MSD (gas chromatography (GC)–mass spectrometry (MS)). An HP-5MS US capillary column (30 m × 250 μm i.d., df = 0.25 μm) from Agilent Technologies was employed for all extraction analyses.

2.3. Synthetic Protocol for the N-Substituted Pyrrole-Based Imidazolium ILs. 2.3.1. 1-(6-Bromohexyl)-1H-pyrrole (2). Pyrrole (1.4 mL, 20 mmol) was added via a syringe pump (KDS 220, KD Scientific, Holliston, MA) at a flow rate of 1.3 mL/h to DMF (200 mL) containing NaH (60% dispersion in mineral oil, 2.40 g, 60 mmol) and anhydrous Na2SO4 and concentrated on a rotary evaporator to remove water. A yellow liquid (0.71 g, 99%) was obtained under vacuum.

1H NMR (600 MHz, CDCl3): δ(ppm) 6.85 (t, J = 2.1 Hz, 2H), 6.14 (t, J = 2.1 Hz, 2H), 3.88 (t, J = 7.0 Hz, 2H), 3.40 (t, J = 6.7 Hz, 2H), 1.87–1.83 (m, 2H), 1.81–1.76 (m, 2H), 1.48–1.44 (m, 2H), 1.33–1.29 (m, 2H) ppm. 13C NMR (150 MHz, CDCl3): δ(ppm) 120.6, 108.1, 101.1, 43.9, 33.9, 31.9, 31.7, 29.2, 26.7, 26.1, 25.8 ppm. HRMS-ESI m/z calcd for C15H15NBr: [M+H]+: 230.0544, found: 230.0538.

2.3.2. General Method for the Synthesis of Pyrrole-Based Imidazolium ILs from Compound 2. 2.3.1. 1-(6-Bromohexyl)-1H-pyrrole and 1 mol equiv of the 1-substituted imidazole derivative were measured in a clean and dry 50 mL round-bottom flask equipped with a water-cooled condenser, followed by the addition of acetonitrile (20 mL) under an Ar purge. The mixture was heated with stirring at 65 °C overnight. The solvent was then removed on a rotary evaporator. The residue was finally triturated with toluene (5 × 20 mL) and dried under vacuum.

2.3.3. 3-(6-(1H-Pyrrol-1-yl)hexyl)-1-methyl-1H-imidazol-3-ium Bromide ([Pyrrole-C6H5Mim]Br) (3). 2.3.1. 1-(6-Bromohexyl)-1H-pyrrole (0.53 g, 2.3 mmol) and 1-methylimidazolide (0.18 g, 2.8 mmol) were used to obtain a yellow viscous liquid (0.71 g, 99%). 1H NMR (600 MHz, CDCl3): δ(ppm) 10.39 (s, 1H), 7.47 (t, J = 1.7 Hz, 1H), 7.38 (t, J = 1.7 Hz, 1H), 6.61 (t, J = 2.1 Hz, 2H), 6.08 (t, J = 2.1 Hz, 2H), 4.28 (t, J = 7.32 Hz, 2H), 4.07 (t, 3H), 3.85 (t, J = 7.0 Hz, 2H), 1.90–1.85 (m, 2H), 1.75–1.70 (m, 2H), 1.34–1.28 (m, 4H) ppm. 13C NMR

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(150 MHz, CDCl3): δ (ppm) 137.6, 123.5, 122.0, 120.6, 107.9, 50.0, 49.4, 36.8, 31.2, 30.2, 26.1, 25.8 ppm. HRMS-ESI m/z calc for C$_{10}$H$_{21}$N$_{4}$: [M$^+$$-$H$^-$]: 232.180, found: 232.181.

2.3.4. 3-(3H-Pyrryl)-1-ethyl)-1 benzyl-1H-imidazolium-3-ium Bromide ([Pyrrole-C$_6$BMIm][Br]) (4), 1-(6-bromohexyl)-1H-pyrrrole (0.55 g, 2.4 mmol) and 1-benzylimidazole (0.46 g, 2.9 mmol) were used to yield 4 (0.92 g, 98%). $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 10.76 (s, 1H), 7.47 (dd, J = 4.1 Hz, 7.9 Hz, 2H), 7.37 (dd, J = 1.6 Hz, 2.0 Hz, 2H), 7.24 (dt, J = 1.8 Hz, 1.7 Hz, 1H), 6.61 (t, J = 2.1 Hz, 2H), 6.10 (t, J = 2.1 Hz, 2H), 5.59 (s, 2H), 4.27 (t, J = 7.5 Hz, 2H), 3.85 (t, J = 6.9 Hz, 2H), 1.94–1.86 (m, 3H), 1.75–1.70 (m, 2H), 1.34–1.29 (m, 4H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): δ (ppm) 137.5, 133.0, 129.7, 129.6, 129.2, 121.9, 121.7, 120.6, 108.0, 53.5, 50.1, 49.4, 31.2, 30.1, 26.1, 25.9 ppm. HRMS-ESI m/z calc for C$_{30}$H$_{32}$N$_{4}$: [M$^+$$-$H$^-$]: 308.2112, found: 308.2122.

2.3.5. General Protocol for Anion Exchange of Br$^-$ to PF$_6$$^-$ IL Derivatives. A 1:1 mixture of the bromide salt of each IL and NH$_4$PF$_6$ was prepared in 20 mL of a 1:1 solution of DI H$_2$O and CH$_3$Cl$_2$ and then stirred vigorously overnight at room temperature under a blanket of Ar. The organic layer was separated, and the solvent was removed on a rotary evaporator. The specific amounts and the analytical data are as given below.

2.3.6. [Pyrrole-C$_6$MIm]PF$_6$ [Pyrrole-C$_6$MIm]Br (3) (0.50 g, 1.6 mmol) and NH$_4$PF$_6$ (0.78 g, 4.8 mmol) were mixed to yield a yellow viscous liquid (0.47 g, 95%). $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 8.89 (s, 1H), 7.20 (t, J = 1.6 Hz, 1H), 7.16 (t, J = 1.6 Hz, 1H), 6.64 (t, J = 2.0 Hz, 2H), 6.11 (t, J = 2.0 Hz, 2H), 4.11 (t, J = 3.3 Hz, 2H), 3.86 (t, J = 7.0 Hz, 2H), 1.87–1.82 (m, 2H), 1.77–1.72 (m, 2H), 1.3–1.27 (m, 4H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): δ (ppm) 136.1, 123.5, 122.0, 120.7, 107.9, 50.0, 49.3, 36.8, 31.2, 30.2, 26.1, 25.8 ppm. HRMS-ESI $m/z$ calc for C$_{30}$H$_{32}$N$_{4}$: $[M^+ - Br^-]$: 315.1711, found: 315.1719.

2.3.7. [Pyrrole-C$_6$BnIm]PF$_6$ [Pyrrole-C$_6$BnIm]Br (4) (0.43 g, 1.4 mmol) and NH$_4$PF$_6$ (0.54 g, 3.3 mmol) were mixed to yield a yellow viscous liquid (0.47 g, 95%). $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 8.89 (s, 1H), 7.40 (dd, J = 1.9 Hz, 2.0 Hz, 2H), 7.36 (dd, J = 3.3 Hz, 2.1 Hz, 2H), 7.15 (t, J = 1.8 Hz, 2H), 7.10 (t, J = 1.8 Hz, 2H), 5.28 (s, 2H), 4.10 (t, J = 7.4 Hz, 2H), 1.86–1.80 (m, 2H), 1.74–1.70 (m, 2H), 1.32–1.26 (m, 4H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): δ (ppm) 135.7, 129.9, 129.8, 129.2, 122.2, 122.0, 120.7, 108.0, 53.8, 50.2, 49.4, 31.2, 29.7, 26.0, 25.6 ppm.

2.4. Fabrication of CPIL-Modified CMEs. For CME fabrication, a 1.6 mm diameter Pt disk electrode was first polished with alumina gamal (<0.1 μm) and sonicated for 5 min (Branson model 1210 ultrasonic bath). The electrode was pretreated in a 0.5 M H$_2$SO$_4$ solution by cycling the potential between −0.2 and +1.0 V (vs Ag/AgCl) until a constant cyclic voltammogram (CV) appeared. The electrode was then washed with DI water and acetone, dried, and placed in an acetonitrile solution containing 0.1 M CPIL-based monomer. Electropolymerization was performed at a constant potential of +1500 mV (vs Ag/AgCl) for 750 s. Finally, the electrode was removed and rinsed with DI water for further experiments.

2.5. Fabrication of CPIL-Modified SPME Fibers. For SPME fiber fabrication, the Pt wire (125 μm diameter) was first assembled as reported previously. The fiber assembly was then washed with DI water, followed by acetone and pretreated in 0.5 M H$_2$SO$_4$. CPIL-based sorbent coatings were then deposited as before using a polymerizing solution that included 10 μL of a 0.6% solution of SWNT in DMA at miciliter of the polymerizing solution. Optical microscopy was then used to ensure a dark film coated the fiber surface.

2.6. Experimental Conditions for Headspace (HS)-SPME Analysis. Standard solutions of the individual analytes were prepared in acetonitrile. Working solutions of 200 μg L$^{-1}$ were made by spiking a certain amount of the standard solution into a 20 mL sample vial containing 15 mL of salt water (30% w/w). All extractions were carried out under HS-SPME conditions at a constant stirring rate (800 rpm) for 30 min. After extraction, thermal desorption was conducted by placing the SPME fiber in the GC inlet at 250 °C for 5 min. Helium was used as the carrier gas with a flow rate of 1 mL min$^{-1}$. The GC column was operated with a separation temperature program from 100 to 200 °C at 5 °C min$^{-1}$, followed by a ramp of 20 °C min$^{-1}$ to 300 °C. GC–MS detection was then accomplished via the selected-ion monitoring mode by monitoring 3 m/z fragment ions for each analyte.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of N-Substituted Pyrrole-Based Imidazolium ILs. The synthesis of pyrrole-based IL monomers was carried out according to a literature-modified synthetic route. As presented in Scheme 1a, two different ILs were synthesized by varying the R substituent on the imidazole head group. For each synthesis, pyrrole (1) was first reacted and coupled with 1,6-dibromohexane to obtain 2. This alkylation was performed under controlled addition of NaH, DMF, 0 °C to RT, 24 h; (ii) acetonitrile, 65 °C, reflux overnight; (iii) NH$_4$PF$_6$ 10 mL of CH$_3$Cl$_2$ and 10 mL of DI water, RT.

Scheme 1. (a) Synthetic Procedure for the N-Substituted Pyrrole-Based Imidazolium ILs; (b) Electropolymerization at a Constant Potential of +1500 mV (vs Ag/AgCl) in Acetonitrile
benzylimidazolium bromide (4) IL monomers by the reaction of imidazole with the relevant R group. In the final step, the exchange of the Br\textsuperscript{−} anion with NH$_4$PF$_6$ afforded the monomers as the PF$_6$\textsuperscript{−} salt. This conversion was confirmed by the $^1$H NMR upfield shift of the most acidic imidazolium proton from about 11.0 to 8.6 ppm. This observation agreed with the anion exchange of similar imidazolium-based ILs.\textsuperscript{34,36}

TGA–DTG data for the [pyrrole-C$_6$MIm]PF$_6$ and [pyrrole-C$_6$BnIm]PF$_6$ monomers are shown in Figure 1. As can be seen, initially, there was a slight loss in mass for both monomers due to residual solvent evaporation. For [pyrrole-C$_6$MIm]PF$_6$, the initial and final exothermic decomposition temperatures were 350 and 470 °C, respectively, whereas for [pyrrole-C$_6$BnIm]PF$_6$ they were 280 and 470 °C, respectively. Also, the onset temperature for the decomposition of [pyrrole-C$_6$MIm]PF$_6$ was significantly higher (425 °C) than that for [pyrrole-C$_6$BnIm]PF$_6$ (365 °C). These values are consistent with the reported values for similar ILs\textsuperscript{33} as well as the analogous thiophene-based IL monomers.\textsuperscript{33} The excellent thermal stability implies that [pyrrole-C$_6$MIm]PF$_6$ is more resistant to higher temperatures than the [pyrrole-C$_6$BnIm]PF$_6$ monomer and will be suitable for high-temperature applications such as SPME, wherein the fibers are exposed to high temperatures in a GC inlet for analyte desorption.

3.2. Preparation and Characterization of Poly[pyrrole-C$_6$MIm]PF$_6$. Electropolymerization of [pyrrole-C$_6$MIm]PF$_6$ was optimized and conducted under controlled potential conditions (+1500 mV vs Ag/AgCl for 750 s) on Pt electrodes of different geometries to obtain the CPIL polymer coating (Scheme 1b). Initial attempts to polymerize the bromide monomer, [pyrrole-C$_6$MIm]Br, did not result in an observable polymer coating on the electrode surface. As reported previously, this could be due to the more ionic nature of the resulting polymer with Br$^\text{−}$ anions.\textsuperscript{33,38} Therefore, to increase hydrophobicity and afford polymerization, metathesis to the PF$_6$\textsuperscript{−} salt was performed before polymerization. Once polymerized, the deposited polymer was rinsed with acetonitrile and dried under atmospheric conditions.

The polymer film was deposited on a Pt flag electrode (0.25 cm$^2$) for in situ FTIR characterization and compared to that of the monomer (Figure S1). It is clearly observed in Figure S1a that the intensity of the absorption due to the out-of-plane bending of the pyrrole C–H bond at around 735 cm$^{-1}$ is greatly reduced in the polymer (Figure S1b). This is indicative of the desirable $\alpha$–$\alpha$ coupling of pyrrole units during polymerization.\textsuperscript{34,39} After electropolymerization, the peaks in the range of 900–1120 cm$^{-1}$ were also not well resolved compared to those of the monomer. This may be attributed to the interactions and steric effects between the adjacent pyrrole rings in the polymer.\textsuperscript{40} Furthermore, absorptions around 2900 and 3100 cm$^{-1}$ due to C–H symmetric and antisymmetric stretching vibrations were observed in both monomer and polymer.\textsuperscript{37} Scanning electron microscopy (SEM) images of the modified flag electrode exhibited an overall uniform surface morphology with a distinct surface wrinkling pattern (see Figure S2). The exact reason for this patterning is unclear; however, it is consistent with other reported substituted pyrrole polymers.\textsuperscript{34}

3.3. Electroanalysis with Poly[pyrrole-C$_6$MIm]PF$_6$-Modified Electrodes. The electrochemical properties of poly[pyrrole-C$_6$MIm]PF$_6$-modified electrodes were also investigated. For this study, the CPIL was first deposited onto a 1.6 mm diameter Pt disk electrode and CVs were recorded in a solution of the anionic redox probe, [Fe(CN)$_6$]$^{3−}$/\textsuperscript{4+}, are presented in Figure 2. Both bare and CPIL-modified Pt electrodes showed well-defined and reversible redox peaks for [Fe(CN)$_6$]$^{3−}$/\textsuperscript{4+} under the same conditions. With a bare Pt electrode, anodic ($E_{pa}$) and cathodic ($E_{pc}$) peak potentials were observed at +245 and +175 mV (\$\Delta E_p \approx 70$ mV, Figure 2a), whereas for the CPIL-modified electrode, $E_{pa}$ was observed at +126 mV and $E_{pc}$ at +4 mV (\$\Delta E_p \approx 122$ mV, Figure 2b). Similarly, formal potentials ($E^\circ$) were observed at +210 mV for an unmodified Pt electrode and at +65 mV for the CPIL-modified Pt electrode, indicating a more favorable oxidation at the modified electrode. Furthermore, when comparing the peak currents of both electrodes, the polymer-modified electrode produced two times the current response of the unmodified electrode, whereas both exhibited peak current ratios, $i_{pa}/i_{pc}$ approximately equal to 1. The increased current is likely due to the electrostatic attraction of the anionic redox probe to the positively charged imidazolium cation moiety. As a result of these findings, and supported by

Figure 1. TGA–DTG analysis of pyrrole-based IL monomers with different substituent groups (heating rate, 10 °C min$^{-1}$).
an effective charge barrier toward cationic species. These observations were consistent with the results reported previously for thiophene-based CPILs.\(^{33}\) Concurrently, control experiments were conducted by polymerizing only pyrrole to prepare polypyrrole-modified electrodes. These films showed a nonselective redox behavior for both \([\text{Co(Sep)}]^3+\) and \([\text{Fe(CN)}_6]^{3–}\) probes (Figures S4 and S5). In both cases, prominent reversible oxidation and reduction peaks were observed. This observation further demonstrates the effect of the imidazolium side chain for ion selectivity.

To test the ion-repulsion hypothesis further, TEMPO, another well-known redox probe was employed.\(^{32,44}\) TEMPO is a heterocyclic radical with intrinsic stability that permits its use in a wide variety of chemical applications.\(^{44}\) As shown in Scheme 2, TEMPO can readily undergo a reversible one-

![Scheme 2. Structure of TEMPO and Its Reversible Oxidation and Reduction Reaction](image)

\[\text{TEMPO} \xrightleftharpoons[+e]{-e} \text{TEMPO}^+\]

electron oxidation and a reduction reaction, wherein, upon oxidation, TEMPO produces a cationic oxoammonium ion (TEMPO\(^+\)). The unique charge characteristics of TEMPO, based on its oxidation state, allow us to investigate the influence of the CPIL coating after electrogeneration of TEMPO\(^+\). CVs for TEMPO redox activity were recorded at different scan rates for the bare (\(E_{pc} = +540\) mV, \(E_{pa} = +475\) mV, \(\Delta E_p = 65\) mV, and \(E_{pa}^o = +508\) mV) and CPIL-modified (\(E_{pc} = +575\) mV, \(E_{pa} = +485\) mV, \(\Delta E_p = 110\), and \(E_{pa}^o = +530\) mV) Pt electrodes. The redox behavior of TEMPO is characterized as diffusion controlled and reversible at the bare Pt electrode for all scan rates tested. The ratio \(i_{pa}/i_{pc}\) is approximately equal to 1, and a linear plot of the square root of scan rate versus peak current (\(R^2 = 0.9995\)) confirmed the reversibility of the redox couple (Figure S6). Similarly, CVs of TEMPO at different scan rates were recorded with a CPIL-modified electrode under the same conditions (Figure S7). At higher scan rates (such as 50 and 100 mV s\(^{-1}\)), TEMPO exhibits a reversible response. However, as the scan rate became lower (<10 mV s\(^{-1}\)), the reversible reduction of electrogenerated TEMPO\(^+\) was less prevalent than the response at the bare Pt electrode (Figure 4). This suggests that if the scan rate is low enough, the repulsion of cationic species from the surface of the electrode hastens the mass transport of TEMPO\(^+\) from the surface of the electrode on this time scale and thereby decreases the peak current for reduction. In contrast, electrodes modified with polypyrrole-C\(_6\)BnIm\]PF\(_6\) did not demonstrate any electrochemical activity toward either \([\text{Co(Sep)}]^3+\) or \([\text{Fe(CN)}_6]^{3–}\), suggesting the formation of a thin insulating layer on the electrode surface (Figures S8 and S9).

### 3.4. SPME with Electrodeposited Poly[pyrrole-C\(_6\)MIm]PF\(_6\) on Microelectrode Substrates

In SPME, uniform film thicknesses with a high fiber-to-fiber reproducibility are considered critically important yet difficult to manage during the fabrication process. Hence, the utilization of electrochemical polymerization to produce highly functional...
modified fiber substrates is advantageous to overcome these challenges. On the basis of our earlier work with thiophene-based IL monomers, the film thickness for SPME analyses was limited to 5 μm, most likely resulting from the reduced conductivity of the growing film despite the conducting nature of the polymer.\(^3\) To improve the conductivity of the growing polymer and achieve thicker films, the new pyrrole-based CPIL monomers were polymerized in the presence of conductive SWNT.

For SPME fiber fabrication, both [pyrrole-C\(_6\)MIm]PF\(_6\) and [pyrrole-C\(_6\)BnIm]PF\(_6\) monomers with SWNT were electro-polymerized on 125 μm Pt wires. The deposition of poly[pyrrole-C\(_6\)MIm]PF\(_6\) on the Pt wire electrode was clearly visible in SEM images as a dense black coating compared to the uncoated wire (Figure 5). In the absence of SWNT, the films were irregular in shape and reached a limit of only 17 μm. In contrast, a good control of the fiber thickness and a uniform coating were achieved with the addition of SWNT. Under the optimum electropolymerization conditions, a film thickness of 42 μm was obtained. Further attempts were made to increase the coating thickness, such as changing the oxidation potential and the electrochemical technique. However, no significant polymer growth beyond 42 μm was observed using these approaches. On the basis of the preliminary experiments, the SWNT concentration in the polymerizing solution had a minimal effect on fiber thickness beyond the optimum conditions. This leveling off in fiber thickness is likely from achieving a maximum loading of SWNT into the polymer matrix. The SPME fibers prepared with [pyrrole-C\(_6\)MIm]PF\(_6\) were washed with acetonitrile and conditioned in the GC inlet at 250 °C for 5 min to remove any residual solvent and unpolymerized monomer.

The addition of SWNT to the [pyrrole-C\(_6\)BnIm]PF\(_6\) monomer polymerization solution did not produce improved film thicknesses. The nonconducting nature of the polymer as evident from the electrochemical study hindered the formation of thicker films even with the addition of SWNT.

3.4.1. SPME Analysis and Comparison with a Commercial PDMS Fiber. The extraction efficiency of the poly[pyrrole-C\(_6\)MIm]PF\(_6\) sorbent coating was evaluated using a series of target analytes, including FAMEs and aromatic compounds, in HS-SPME analysis. HS extraction as a function of time was performed to generate sorption-time profiles to determine the equilibration time for all analytes on the SPME sorbent coating. As shown in Figure S10, equilibration was reached in approximately 30 min for most analytes. Thus, an extraction time of 30 min was used for all subsequent studies.

As can be seen in Figure 6, an excellent fiber-to-fiber reproducibility was achieved with the SWNT-doped poly[pyrrole-C\(_6\)MIm]PF\(_6\) coatings, further supporting the reliability of electropolymerization as an effective SPME coating fabrication technique. It was also observed in Figure 6 that the CPIL fibers are more selective toward aromatic compounds over the other polar analytes, which is likely due to the combination of the CPIL with SWNT, as previously reported.\(^24\),\(^45\),\(^47\) The distinct SWNT structure together with the CPIL permits interactions with aromatic compounds, such as PAHs, via π−π interactions.\(^48\) There are several other benefits of incorporating SWNT, such as achieving a high electroactive surface area and a high thermal stability. SWNT can also facilitate the orientation of imidazolium ions with possible cation−π interactions.\(^49\),\(^50\) This may trigger a proper ordering of imidazolium side chains on the polypyrrole backbone with increasing thickness and mechanical strength of the fiber coating. For these experiments, SWNT clearly assist in the reproducible preparation of thicker CPIL sorbent coatings and the extraction of organic aromatic analytes.

For comparison, the extraction of the same analytes was performed using a commercial 100 μm PDMS fiber. Figure 7 demonstrates that the PDMS fiber exhibited a higher extraction efficiency for all analytes compared to that of poly[pyrrole-C\(_6\)MIm]PF\(_6\)/SWNT fibers. However, it is also worth noting that the film thickness of the PDMS fiber is significantly greater than that of the poly[pyrrole-C\(_6\)MIm]PF\(_6\)/SWNT coating. The higher extraction efficiency of the PDMS fiber can be due to the higher extraction phase volume. To better evaluate the

![Figure 4](Image)

Figure 4. CVs of an aqueous solution of 10 mM TEMPO with 0.1 M KNO\(_3\) at (a) a bare Pt electrode and (b) a poly[pyrrole-C\(_6\)MIm]PF\(_6\)-modified electrode. The scan rate is 10 mV s\(^{-1}\). Initial potential: 100 mV; scan direction to positive potentials.

![Figure 5](Image)

Figure 5. SEM images of (A) an uncoated 125 μm Pt wire, (B) a Pt wire modified with poly[pyrrole-C\(_6\)MIm]PF\(_6\), and (C) a Pt wire modified with poly[pyrrole-C\(_6\)MIm]PF\(_6\)/SWNT.
Figure 6. Comparison of the fiber-to-fiber reproducibility for poly[pyrrole-C6MIm]PF6/SWNT-coated fibers under the same extraction conditions. Each analyte was dissolved in 30% salt water at 200 μg L⁻¹.

Figure 7. Comparison of response between a commercially available PDMS fiber and poly[pyrrole-C6MIm]PF6/SWNT-coated fibers under the same extraction conditions. Each analyte was dissolved in 30% salt water at 200 μg L⁻¹.

Figure 8. Comparison of normalized response between a commercially available PDMS fiber and poly[pyrrole-C6MIm]PF6/SWNT-coated fibers under the same extraction conditions. Each analyte was dissolved in 30% salt water at 200 μg L⁻¹.
4. CONCLUSIONS

CPIL coatings on different electrode substrates were achieved by the electropolymerization of [pyrrole-C6MIm][PF6] which exhibited excellent control over the deposition parameters and provided uniform film thicknesses. Electrochemical investigations revealed that the polymer was more selective for anionic species and acted as an electrostatic repulsion barrier for cationic species. This was consistent with the results previously reported for thiophene-based CPIL coatings. Coatings made with [pyrrole-C6MIm][PF6] and doped with SWNT showed a much improved thickness (42 vs 5 μm with thiophene-based CPILs) when electropolymerized for SPME analysis. A successful application in HS-SPME indicated that the CPIL coatings on different electrode substrates were achieved by the electropolymerization of [pyrrole-C6MIm][PF6] which exhibited excellent control over the deposition parameters and provided uniform film thicknesses. Electrochemical investigations revealed that the polymer was more selective for anionic species and acted as an electrostatic repulsion barrier for cationic species. This was consistent with the results previously reported for thiophene-based CPIL coatings. Coatings made with [pyrrole-C6MIm][PF6] and doped with SWNT showed a much improved thickness (42 vs 5 μm with thiophene-based CPILs) when electropolymerized for SPME analysis.

REFERENCES


