# Preparation and Characterization of Poly[2,3-dimethyl-1-(4-thien-3-ylbenzyl)-1*H*-imidazol-3-ium] Bis((trifluoromethyl)sulfonyl)imide

# Eric Naudin,<sup>†</sup> Hoang Anh Ho,<sup>‡</sup> Marc-André Bonin,<sup>‡</sup> Livain Breau,<sup>\*,‡</sup> and Daniel Bélanger<sup>\*,†</sup>

Département de Chimie, Université du Québec à Montréal (UQAM), Case Postale 8888, succursale Centre-Ville, Montréal, Québec, Canada H3C 3P8, and Laboratoire de Synthèse Organique Appliquée, Département de Chimie, UQAM, Case Postale 8888, succursale Centre-Ville, Montréal, Québec, Canada H3C 3P8

Received July 13, 2001; Revised Manuscript Received April 3, 2002

ABSTRACT: A new 3-fluorophenylthiophene derivative bearing a cationic imidazolium group in the para position of the phenyl ring was synthesized by a multistep procedure which involves, in a key step, the reaction of 3-[4-(bromomethyl)phenyl]thiophene with 1,2-dimethylimidazole. The bis[(trifluoromethyl)sulfonyl]imide (TFSI) salt was obtained by anion exchange of the imidazolium bromide precursor with LiTFSI. The electrochemical oxidation of the title monomer in dichloromethane afforded an electronically conducting polymer displaying both p- and n-doping redox waves. These redox processes were also accompanied by change in absorption spectra that confirmed the modification of the electronic properties of the polymer upon both p- and n-doping.

#### Introduction

In the past 20 years, considerable effort has been devoted to the electrochemical study of electronically conducting polymers such as polypyrrole, polyaniline, and polythiophene. These conducting polymers have attracted great interest due to their potential use as electrode materials in electrochromic devices, sensors, light-emitting diodes, batteries, and supercapacitors.<sup>1</sup>

An interesting class of conducting polymers is the socalled self-doped polymers for which the charge-compensating ion is covalently bound to the polymer backbone.<sup>2–8</sup> The first self-doped polymers used sulfonate groups as ionic sites and part of the substituents of polythiophene derivatives.<sup>3</sup> An interesting characteristic of these polymers, compared to their counterpart having no such ionic sites, is that the charge compensation upon electrochemical oxidation involves the expulsion of cationic species instead of anion incorporation. The presence of an ionic group on the polymer backbone can also impart solubility properties to the polymer in both the doped and undoped states. In addition, charged redox active sites were also incorporated on the polymer backbone.<sup>6</sup>

In our laboratory, we are interested in evaluating conducting polymers as active electrode materials for electrochemical supercapacitors.<sup>9</sup> The use of self-doped polymers for this purpose is limited to a polythiophene derivative having a trimethylammonium group in the para position of 3-phenylthiophene.<sup>10</sup> Such a polymer having a positively charged group covalently bound to the thiophene unit is very interesting since charge compensation in both the n- and p-doped states should only involve anionic species. Consequently, problems associated with depletion of salt from the electrolyte for

polymers having cations and anions ingress during nand p-doping, respectively should be solved.<sup>11</sup>

In this work, we report the synthesis of a 3-phenylthiophene derivative having an imidazolium group in the para position on the phenyl ring (**8** in Scheme 1) and preliminary electrochemical (cyclic voltammetry) and spectroscopic (UV–vis) studies of the electrochemical generated polymer. Interestingly, this ionic group forms ionic liquid in the presence of an appropriate anions,<sup>12</sup> and therefore, it might interesting to prepare a polymer having a substituent which is the cationic species of a salt. Such polymer might be also useful for application requiring the presence of permanent positive charge on the polymer backbone.

# **Experimental Section**

**Chemicals and Electrodes.** Acetonitrile (HPLC grade) was used as received. Tetraethylammonium bis((trifluoromethyl)sulfonyl)imide (Et<sub>4</sub>NTFSI) was synthesized from lithium bis((trifluoromethyl)sulfonyl)imide (used as-received from 3M) and tetraethylammonium bromide (Aldrich Chemical Co.). 3-Bromothiophene, 4-bromobenzyl alcohol, *tert*-butyldimethylsilyl chloride (TBDMSCI), tetrabutylammonium fluoride hydrate, phosphorus tribromide, imidazole, and 1,2-dimethylimidazole were obtained from Aldrich Chemical Co. and were used without further purification. THF and diethyl ether were dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior use. All reactions involving organometallic reagents were carried out under nitrogen.

A 1 mm diameter platinum disk and platinum gauze were used as working and counter electrode, respectively. The Pt disk electrode was polished with 0.05  $\mu$ m alumina slurry (Buehler) and washed with water and cleaned ultrasonically before use. A transparent tin oxide-coated glass electrode was used for the spectroscopic measurements of the polymer. Prior to polymer deposition, the transparent electrode was cleaned by soaking in a 1 M HNO<sub>3</sub> aqueous solution for 1 h. All potentials were referenced against a  $10^{-2}$  M Ag<sup>+</sup>/Ag electrode.

**Synthesis.** The monomer **8** was prepared via a Kumada<sup>13</sup> coupling reaction and was an adaptation of our previously published procedure for ionic liquid<sup>12</sup> (Scheme 1).

<sup>&</sup>lt;sup>†</sup> Département de Chimie.

<sup>&</sup>lt;sup>‡</sup> Laboratoire de Synthèse Organique Appliquée, Département de Chimie.

<sup>\*</sup> To whom all correspondence should be sent. E-mail: belanger.daniel@uqam.ca; breau.livain@uqam.ca.



[(4-Bromobenzyl)oxy](tert-butyldimethyl)silane (2). To a solution of 4-bromobenzyl alcohol, 1 (5.00 g, 26.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL), was added imidazole (1.93 g, 28.3 mmol) followed by TBDMSCl (4.27 g, 28.3 mmol) in three portions. The mixture was stirred for 45 min and quenched by the addition of Na<sub>2</sub>CO<sub>3</sub> (10%), stirred for 20 min, and extracted in  $CH_2Cl_2$  (3  $\times$  50 mL). The combined organic extracts were washed with brine (20 mL), dried over MgSO<sub>4</sub>, filtered, and evaporated. The crude yellow mass was dissolved into petroleum ether (40 mL), filtered, evaporated, and Kugelrohr distilled, affording 7.15 g (89%) of 2 as a colorless oil; bp 131 °C (3 mmHg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.46 (dt, J =8.5, 1.9 Hz, 2H, H-3 + 5), 7.22 (bd, J = 8.5 Hz, 2H, H-2 + 6), 4.71 (s, 2H, CH<sub>2</sub>O), 0.96 (s, 9H,  $3 \times CH_3$ -C), and 0.12 (s, 6H, 2 × CH<sub>3</sub>-Si). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>, ppm): 140.40 (C), 131.23 (2 CH), 127.67 (2 CH), 120.54 (C), 64.27 (CH<sub>2</sub>), 25.88 (3 CH<sub>3</sub>), 18.34 (C), -5.31 (2 CH<sub>3</sub>-Si). GC-MS (70 eV) m/z (rel int): 302 (1%, M<sup>+81</sup>Br); 300 (1%, M<sup>+79</sup>Br); 245 (100%, <sup>81</sup>Br); 243 (100%, 79Br), 215 (26%, M+81Br); 213 (26%, M+79Br), 171 (47%, <sup>81</sup>Br); 169 (47%, <sup>79</sup>Br), and 90 (10%).

tert-Butyldimethyl[4-thien-3-ylbenzyl)oxy]silane (4). A solution of 4-benzyloxy-(tert-butyldimethyl)silylmagnesium bromide, 3, was freshly prepared from [(4-bromobenzyl)oxy]-(tert-butyldimethyl)silane (2) (0.904 g, 3.0 mmol) and magnesium turnings (0.108 g, 4.5 mmol) in refluxing tetrahydrofuran (10 mL) for 2 h. After cooling the Grignard reagent 3 to room temperature, 3-bromothiophene (0.28 mL, 3.0 mmol) was added along with NiCl<sub>2</sub>(dppe) (55 mg, 0.10 mmol), which was added four times at intervals of 5 min. The mixture was refluxed for 3 h and then was carefully hydrolyzed with H<sub>2</sub>O (5 mL) followed by ammonium chloride saturated solution (25 mL). The mixture was diluted with ether (40 mL), and the organic layer was separated. The aqueous layer was extracted with ether  $(3 \times 15 \text{ mL})$ , and the combined organic layers were dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure, and the dark crude residue was purified on a plug of silica gel (5 g) using petroleum ether. The yellow mass thus obtained was separated on silica gel (chromatotron,  $2 \times 4$  mm, petroleum ether) to afford 610 mg (67%) of the title compound, 4, as a colorless crystalline solid; mp: 76–79 °C. IR (cm<sup>-1</sup>): 3092, 2925, 2850, 1466, 1255, 1097, 1051, 864, 836, 776, and 767. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.59 (bd, J = 8.4 Hz, 2H, H-3,+ 5), 7.45 (dd, J = 2.2,  $\hat{1.9}$  Hz, 1H, H-2'), 7.41-7.39 (m, 2H, H-4', +5'), 7.37 (d, J = 8.4 Hz, 2H, H-2 +6), 4.78 (s, 2H, CH<sub>2</sub>O), 0.98 (s, 9H, 3  $\times$  CH<sub>3</sub>–C) 0.72 (s, 1H, OH), and 0.13 (s, 6H, 2 × CH<sub>3</sub>-Si). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>, ppm): 142.24 (C), 140.36 (C), 134.50 (C), 126.50 (2 CH), 126.33 (CH), 126.28 (2 CH), 126.10 (CH), 119.96 (CH), 64.74 (CH<sub>2</sub>), 25.96 (3 CH<sub>3</sub>), 18.42 (C), -5.23 (2 CH<sub>3</sub>-Si). GC-MS (70 eV) m/z (rel int): 304 (M<sup>+</sup> 2), 247 (22), 173 (100).

**(4-Thien-3-ylphenyl)methanol (5).** A solution of **4** (530 mg, 1.74 mmol) in THF (10 mL) was treated with  $Bu_4NF \cdot H_2O$  (820 mg), and the mixture was stirred at 25 °C for 45 min. The resultant solution was diluted with water (25 mL) and EtOAc (25 mL). The phases were separated, and the aqueous one was extracted with EtOAc (3 × 15 mL). The combined organic extract were dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo. Chromatography (chromatotron, SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/

EtOAc, 95:5) provided **5** (310 mg, 1.63 mmol, 94%) as a white shiny solid; mp 154–155 °C. IR (cm<sup>-1</sup>): 3315, 3216, 3095, 2912, 2855, 1046, 1011, 866, 824, 774 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.61 (dt, J = 8.2, 1.9 Hz, 2H, H-3), 7.47 (t, J = 2.2 Hz, 1H, H-2'), 7.42 (m, 4H, H-3 + 4,5), 4.73 (s, 2H, CH<sub>2</sub>O), and 1.72 (s, 1H, OH). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>, ppm): 141.95 (C), 139.68 (C), 135.27(C), 127.49 (2 CH), 126.60 (2CH), 126.28 (CH), 126.26 (CH), 120.30 (CH), and 65.11 (CH<sub>2</sub>OH). GC-MS (70 eV) m/z (rel int): 190 (M<sup>+</sup> 100), 173 (25), 161 (60), 128 (45), 115 (29), and 77 (9). Anal. Calcd for C<sub>11</sub>H<sub>10</sub>S: C, 69.4; H, 5.30; S, 16.85. Found: C, 69.10; H, 5.38; S, 16.83.

**3-[4-(Bromomethyl)phenyl]thiophene (6).** To a stirred solution of [4-(3-thienyl)phenyl]methanol (5) (0.64 g, 3.36 mmol) in 20 mL of freshly distilled ether held at 0 °C was added, dropwise, phosphorus tribromide (0.95 mL, 10 mmol). The mixture was then stirred at room temperature for 24 h at which time was added a saturated aqueous solution of sodium carbonate (20 mL). The aqueous layer was extracted with ether, and the combined ethereal layers were washed with water, dried (MgSO<sub>4</sub>), filtered, and evaporated under reduced pressure to yield 0.43 g (51%) of **6** as a white powder.

<sup>1</sup>H NMR (CD<sub>3</sub>Cl)  $\delta$ : 7.58 (dt, J = 8; 2 Hz, 2H); 7.47 (dd, J = 2.6; 1.6 Hz, 1H); 7.44 (dt, J = 8; 2 Hz, 2H); 7.4 (d, J = 2.6 Hz, 1H); 7.39 (d, J = 1.6 Hz, 1H); 4.54 (s, 2H). <sup>13</sup>C NMR (CD<sub>3</sub>-Cl)  $\delta$ : 141.60; 136.54; 135.99; 129.55 (2C); 126.80 (2C); 126.40; 126.22; 120.74; 33.41. GC-MS (70 eV) m/z (rel int): 254 (3%, M<sup>+81</sup>Br); 252 (3%, M<sup>+79</sup>Br); 173 (100%, M<sup>+</sup> – Br,), 128 (8%), 86 (10%).

**2,3-Dimethyl-1-(4-thien-3-ylbenzyl)-1***H***-imidazol-3-ium Bromide (7).** A solution of **6** (0.21 g, 0.83 mmol) and 1,2-dimethylimidazole (0.09 g, 0.91 mmol) in toluene (10 mL), was refluxed for 3 h, and the white crystals formed were decanted from the hot solution. The toluene phase was removed via cannula. The solid product was washed four times with ethyl acetate and dried under reduced pressure to yield 0.29 g (100%) of 7 as a white powder.

<sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$ : 7.89 (dd, J = 2.8; 1.4 Hz, 1H); 7.74 (m, 3H); 7.64 (m, 2H); 7.55 (dd, J = 5.1; 1.4 Hz, 1H); 7.36 (d, J = 8 Hz, 2H); 5.41 (s, 2H); 3.75 (s, 3H); 2.60 (s, 3H).

**2,3-Dimethyl-1-(4-thien-3-ylbenzyl)-1***H***-imidazol-3-ium Bis((trifluoromethyl)sulfonyl)imide (8).** To a stirred solution of 7 (0.29 g, 0.83 mmol) in deionized water (6 mL) was added lithium bis((trifluoromethyl)sulfonyl)imide (0.26 g, 0.91 mmol). The reaction mixture was refluxed for 4 h. The white powder was decanted, filtered, washed four times with deionized water, and then dried over  $P_2O_5$  under reduced pressure to yield 0.34 g (75%) of 8 as a white powder.

UV (DMSO)  $\lambda_{\text{max}}$ : 267 nm. <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$ : 7.89 (dd, J = 3.0; 1.4; Hz, 1H); 7.74 (d, J = 8 Hz, 2H); 7.71 (d, J = 2.2 Hz, 1H); 7.64 (m, 2H); 7.55 (dd, J = 5.2; 1.4 Hz, 1H); 7.35 (d, J = 8 Hz, 2H); 5.44 (s, 2H); 3.81 (s, 3H); 2.62 (s, 3H). <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$ : 144.88; 140.90; 135.56; 133.51; 128.69 (2C); 127.57; 126.82 (2C); 126.39; 122.93; 121.80; 121.46; 119.50 (q,  $J_{C-F} = 320$  Hz, 2C); 50.59; 35.07; 9.71. Anal. Calcd for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>F<sub>6</sub>S<sub>3</sub>: C, 39.34; H, 3.12; N, 7.65; S, 17.5. Found: C, 39.33; H, 2.98; N, 7.68; S, 17.7.

**Procedure and Apparatus.** Polymer films were prepared galvanostatically on a Pt disk by anodic oxidation at an

appropriate current density from a monomer solution in dichloromethane or acetonitrile containing 0.5 M Et<sub>4</sub>NTFSI. The electrochemical studies were performed with an electrochemical cell inside a drybox by using a potentiostat model 1287 Solartron electrochemical interface coupled to a PC with Corrware Software for Windows (Scribner Associates, version 2.1b).

<sup>1</sup>H NMR spectra were recorded using a Varian 300 MHz spectrometer. Chemical shifts are reported in parts per million  $(\delta)$ , and the signals were designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Mass spectra were obtained using a GC-MS (GCD plus gas chromatography-electron ionization detector, HPG 1800A GCD system) equipped with a 5% cross-linked Ph Me silicone HP 19091 J-433 column. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR instrument. Separations were carried out on silica gel (7749 Merck) using circular chromatography (chromatotron, model 7924, Harrison Research). In situ UV-vis spectra were measured with a Hewlett-Packard spectrophotometer (model HP 8452A). For the spectroscopic measurements, the polymer was electrochemically grown on a tin oxide-coated glass electrode at a current density of 14 mA/cm<sup>2</sup> from a 82 mM monomer solution containing 0.5 M Et<sub>4</sub>NTFSI in dichloromethane.

### **Results and Discussion**

Electrochemical Oxidation of the Monomer. The electrochemical oxidation of the monomer salt 8 (82 mM) at a platinum electrode was investigated by cyclic voltammetry at a scan rate of 50 mV/s in nonaqueous media (acetonitrile or dichloromethane) containing 0.5 M TEATFSI. The first cyclic voltammogram in dichloromethane shows an irreversible anodic wave at 1.49 V, which corresponds to the formation of the cation radical. The oxidation potential can be also obtained from the potential-time curve recorded during galvanostatic deposition. In this case, the oxidation potential varies from 1.28 V for a deposition current density of 0.3 mA/ cm<sup>2</sup> to 1.41 V for 1.2 mA/cm<sup>2</sup>. These values are noticeably higher than those found for 3-phenylthiophene<sup>9e,14</sup> and reflects the steric and inductive effects of the imidazolium substituent. In a recent study on substituted 3-arylthiophene, the variation of the oxidation potential of the monomer was explained by the resonance and inductive effects of the substituents (e.g., methyl, fluorine, methylsulfonyl) on the phenyl ring.<sup>14</sup> The inductive effect of the imidazolium group could be operative despite the presence of the intervening methylene group that linked it to the phenyl ring. The oxidation potential of monomer 8 is significantly more positive than that reported for a strong EWG group, suggesting that steric effects might be significant. Thus, the observed shift of the oxidation potential of the monomer can be explained by both inductive and steric effects of the imidazolium moiety. In addition, the counterion (TFSI<sup>-</sup>) of the cationic thiophene monomer 8 may also contribute to the steric effect, especially if the monomer salt is not completely dissociated. This is suggested by the lower oxidation potential (1.35 V) for monomer 8 oxidation in acetonitrile which has a higher dielectric constant than dichloromethane.

Figure 1 shows successive cyclic voltammograms between 0 and 1.4 V with the onset of monomer oxidation at about 1.3 V. On the return scan, a reduction wave is apparent at 0.64 V and is attributed to the reduction of the polymer that was formed on the forward scan. On the second scan, the oxidation of the polymer gives rise to an additional anodic wave at 0.65 V. Both polymer waves grow upon continuous cycling, indicating



**Figure 1.** Cyclic voltammetry for the monomer (82 mM) at a platinum electrode in 0.5 M TEATFSI/dichloromethane. Scan rate = 50 mV/s. The cycle numbers of the successive cyclic voltammograms are indicated in the figure.



**Figure 2.** Cyclic voltammogram for poly-**8** in 0.5 M Et<sub>4</sub>NTFSI/ dichloromethane at a scan rate of 100 mV/s.

the deposition of a polymer at the electrode surface. Finally, a stable polymer film cannot be grown in acetonitrile due to the high solubility of the oligomers which prevented polymer formation.

**Electrochemistry of the Polymer.** Figure 2 shows the cyclic voltammogram for poly-8 in 0.5 M Et<sub>4</sub>NTFSI/ dichloromethane that is characterized by the redox waves centered for p-doping at 0.65 V and n-doping at -2.0 V. The cyclic voltammogram of poly-8, grown in dichloromethane and transferred in acetonitrile, is similar to that of Figure 2 although a quick decay of the redox waves is observed upon potential cycling. In comparison to PPT or PFPT, the redox waves potential are barely affected for poly-8. This is to be contrasted with the difference noted above for the oxidation of the corresponding monomers. A similar trend was recently noticed for a series of substituted arylthiophene and poly(arylthiophene)s.<sup>14</sup> The electrochemical band gap of about 1.7 eV that could be deduced from the difference between the onset of the p- and n-doping is in reasonably good agreement with that of PPT.<sup>9e</sup> The fact that



**Figure 3.** In situ absorption spectra dependence on applied potential for poly-**8** on a tin oxide electrode in 0.5 M Et<sub>4</sub>NTFSI/ dichloromethane. The oxidation potential ranged from 0.1 to 0.9 V vs Ag/Ag<sup>+</sup>.



**Figure 4.** In situ absorption spectra dependence on applied potential for poly-**8** on a tin oxide electrode in 0.5 M Et<sub>4</sub>NTFSI/ dichloromethane. The reduction potential ranged from -1.5 to -2.3 V vs Ag/Ag<sup>+</sup>.

similar band gap values are found for PPT and poly-**8** may seem at odd with the cyclic voltammetry data of the monomer and the spectroscopic data. However, the higher oxidation potential and reactivity of monomer **8** in comparison to 3-phenylthiophene apparently led to polymers with similar conjugation length despite the steric demand of the imidazolium group.

A meaningful doping level could not be determined due to the low polymerization efficiency that is evidenced by the formation of highly colored oligomers diffusing in the deposition solution. The well-defined prepeaks that are clearly observed at 0.09 and -1.72 V are absent when the potential cycling is limited to only the p- or n-doping states. The presence of these prepeaks on the cyclic voltammogram of polythiophene derivatives is well documented in the literature<sup>9a,b,15</sup> and will not be discussed further here.

UV-vis Spectroscopy of the Polymer for the pand n-Doped States. Figures 3 and 4 show a series of in-situ absorbance spectra of poly-8 films on a tin oxide electrode in 0.5 M Et<sub>4</sub>NTFSI/dichloromethane taken at different applied voltages for both the p- and n-doped states, respectively. The neutral films (applied potential of 0.1 and -1.5 V) have an absorption maximum around 515 nm, which is attributed to the  $\pi$ - $\pi$ \* transition of the polymer. The oscillator strength of this band decreases upon increasing the oxidation potential, but another transition is observed at lower energy (around 800 nm). Also, the peak at 515 nm shifts toward higher energy by increasing the oxidation level. Such modifications of the spectra are commonly observed for polythiophene derivatives and are related to the formation of radical cations and dimerized radical cations upon oxidation of the polymer.<sup>16–18</sup> Similar features are seen in the absorption spectra during the reduction of the polymer (Figure 4), but a close look at the evolution of the spectra with electrode potentials revealed some differences. A decrease of the intensity of the main absorption band is noticed upon reduction. On the other hand, and in contrast to what was observed for the p-doped state, the main transition shifts to lower energy, and the bleaching of this band is not as complete. Also, no well-defined band seems to be apparent above 650 nm despite that a constant increase of absorbance is found in this spectral region. These observations indicate that the n-doped polarons are relatively unstable compared to the p-doped polarons. The optical band gap was also evaluated by considering the onset of the  $\pi - \pi^*$ transition.<sup>9e</sup> A value of 1.7 eV was determined and is in very good agreement with that obtained from the electrochemical data.

## Conclusion

In this work, we have shown that a bis(trifluoromethyl)sulfonyl)imide salt of a 3-phenylthiophene derivative bearing a positively charged imidazolium group can be oxidized in dichloromethane to yield an electroactive polymer. The resulting polymer displayed both p- and n-doping redox activity. The presence of a permanent positive charge on the polymer may be useful for the development of electrochemical supercapacitors where charge compensation of the oxidized or reduced may be mainly achieved by anions from the supporting electrolyte.<sup>10</sup> In a recent study, Ferraris and co-workers have presented cyclic voltammetry and electrochemical quartz crystal microbalance studies for a poly(3-phenylthiophene) derivative having a trimethylammonium substituent in the para position.<sup>10a</sup> Their data suggest that anions are primarily involved in the charge compensation mechanism as mass loss and mass gain have been recorded during n- and p-doping, respectively. Further studies on charge transport and conductivity of the polymer will be required to get more insight into the usefulness of poly-8 for some potential applications.

Acknowledgment. This work was partially supported by Strategic and Research Grants from the Natural Sciences and Engineering Research Council (NSERC) of Canada and from "le Fonds FCAR-Soutien aux Equipes" of the Québec government. M.-A.B. thanks NSERC for the award of an Undergraduate Student Research fellowship, and E.N. also acknowledges the financial contribution of UQAM for a fellowship.

#### **References and Notes**

(a) Handbook of Conducting Polymers; Skotheim, T., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.
 (b) Handbook of Organic Conductive Molecules and Polymers: Transport, Photophysics and Applications; Nalwa, H. S., Ed.; Wiley: New York, 1997; Vol. 4. (c) Conway,

B. E. *Electrochemical Supercapacitors*, Kluwer Academic/ Plenum: New York, 1999.

- (2) (a) Roncali, J. In *Handbook of Conducting Polymers*; Skotheim, T., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; Chapter 12, pp 311–341. (b) Ferraris, J. P.; Guerrero, D. J. In *Handbook of Conducting Polymers*; Skotheim, T., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; Chapter 10, pp 259–276.
- Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.
   Ikenoue, Y.; Saida, Y.; Kira, M.-a.; Tomozawa, H.; Yahima, J. *Glassical and Stranger and Stran*
- (4) Ikenoue, Y.; Saida, Y.; Kira, M.-a.; Tomozawa, H.; Yahima, H.; Kobayashi, M. J. Chem. Soc., Chem. Commun. 1990, 1694.
- (5) Bäuerle, P.; Gaudl, K.-U.; Würthner, F.; Sariciftci, N. S.; Neugebauer, H.; Mehring, M.; Zhong, C.; Doblhofer, K. Adv. Mater. 1990, 2, 490.
- (6) Hable, C. T.; Crooks, R. M.; Valentine, J. R.; Giasson, R.; Wrighton, M. S. J. Phys. Chem. 1993, 97, 6060.
- (7) Hua, M.-Y.; Yang, S.-W.; Chen, S.-A. Chem. Mater. 1997, 9, 2750.
- (8) Zotti, G.; Zecchin, S.; Berlin, A.; Schiavon, G.; Giro, G. Chem. Mater. 2001, 13, 43.
- (9) (a) Fusalba, F.; El Mehdi, N.; Breau, L.; Bélanger, D. Chem. Mater. 1999, 11, 2743. (b) Fusalba, Ho, H. A.; Breau, L.; Bélanger, D. Chem. Mater. 2000, 12, 2581. (c) Fusalba, F.; Gouérec, P.; Villers, D.; Bélanger, D. J. Electrochem. Soc.

**2000**, *148*, A1. (d) Soudan, P.; Lucas, P.; Ho, H. A.; Jobin, D.; Breau, L.; Bélanger, D. J. Mater. Chem. **2001**, *11*, 773. (e) Naudin, E.; El Mehdi, N.; Soucy, C.; Breau, L.; Bélanger, D. Chem. Mater. **2001**, *13*, 634. (f) Soudan, P.; Ho, H. A.; Breau L. Bélanger, D. *I. Electrochem. Soc.* **2001**, *148*, A775

- Breau, L. Bélanger, D. J. Electrochem. Soc. 2001, 148, A775.
  (10) (a) Ferraris, J. P. In 7th International Seminar on Double Layer Capacitors and Similar Energy Devices; Wolsky, S. P., Marincic, N., Eds.; Deerfield Beach, FL, Dec 8–10, 1997. (b) Loveday, D. C.; Hmyene, M.; Ferraris, J. P. Synth. Met. 1997, 84, 245.
- (11) Zheng, J. P.; Huang, J.; Jow, T. R. J. Electrochem. Soc. 1997, 144, 2026.
- (12) Lucas, P.; El Mehdi, N.; Ho, H. A.; Bélanger, D.; Breau, L. Synthesis 2000, 9, 1253.
- (13) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.
- (14) Guerrero, D. J.; Ren, X.; Ferraris, J. P. *Chem. Mater.* **1994**, *6*, 1437.
- (15) Zotti, G.; Schiavon, G.; Zecchin, S. *Synth. Met.* **1995**, *72*, 275.
  (16) Donnat-Bouillud, A.; Mazerolle, L.; Gagnon, P.; Goldenberg,
- L.; Petty, M. C.; Leclerc, M. Chem. Mater. 1997, 9, 2815.
- (17) Agrawal, A. K.; Jenekhe, S. A. Chem. Mater. 1996, 8, 579.
- (18) Ferraris, J. P.; Henderson, C.; Torres, D.; Meeker, D. Synth. Met. 1995, 72, 147.

MA011227X