Synthesis, Characterization, and Oxidative Polymerization of 3-(Fluoromethyl)thiophenes

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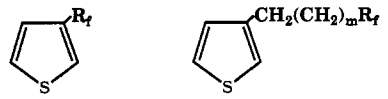
The preparation of 3-(perfluoroalkyl)- (structure 1) and 3-(polyfluoroalkyl)- (structure 2) thiophenes has recently become a topic of great interest because of the promise for these compounds as precursors to conductive polythiophene films. The fluorinated polymers are anticipated to possess improved chemical and thermal stabilities over the nonfluorinated alkyl analogs. We are currently involved in the synthesis, characterization, and electropolymerization of a number of 3-(perfluoroalkyl)- and 3-(polyfluoroalkyl)thiophenes.



(1) (2) (3)

R_f = $-(CF_2)_nCF_3$
m, n ≥ 0

R = $-CH_2F$, $-CHF_2$, $-CF_3$

This communication is prompted by a very recent report (Büchner et al.)[1] describing the synthesis of 3-(difluoromethyl)thiophene by the reaction of 3-thiophenecarboxaldehyde with (diethylamino)sulfur trifluoride (DAST). In their paper, the syntheses of other 3-polyfluorinated thiophenes are also presented. We have previously reported the synthesis of 3-(difluoromethyl)thiophene by the same method.[2] At this time, we wish to communicate our results on the preparation and polymerization of 3-(difluoromethyl)thiophene along with some preliminary results concerning other 3-fluorinated thiophenes. We plan a complete report on this work in the near future.

In an earlier paper, Büchner et al.[3] reported that the preparation of poly(3-(polyfluoroalkyl)thiophenes) by electrooxidation requires the existence of $-CH_2-$ spacer groups between the thiophene ring and the fluorinated alkyl group (see structure 2). A thiophene monomer with two $-CH_2-$ spacers ($m = 1$) between a perfluorohexyl group ($n = 5$) and the ring resulted in a black deposit on the electrode, while thiophene monomers with three $-CH_2-$ spacer groups ($m = 2$) between perfluorobutyl ($n = 3$) or perfluorohexyl groups and the ring gave high-quality free-standing polymer films. Oxidation potentials of the fluorinated monomers and the conductivities of the free-standing polymer films were all reported to be comparable to those of the 3-alkylthiophene analogs. More recently, Ho-Hoang et al.[4] have prepared and successfully polymerized 3-(trifluoroethyl)pyrrole, a monomer with one $-CH_2-$ spacer group. The need for the spacer groups was attributed to the inhibition of polymer formation by the presence of an electronegative, fluorinated group near the aromatic ring. Apparently, experiments with fluorinated groups immediately attached to the ring have not been carried out. The results of Büchner et al.[3] seemed to us somewhat surprising in that a high quality polymer film was not formed from the monomer with two $-CH_2-$ spacer groups, considering the similarity of the Hammett substitutent constants[5] (σ) of alkyl groups with those of the corresponding polyfluoroalkyl groups. To study these substituent effects, we chose a series of fluorinated 3-methylthiophene derivatives (structure 3) in which there is a gradual increase in the electron-withdrawing power of the side chain.

An increase in the number of fluorine atoms in the methyl group is anticipated to result in a progressive increase in the oxidation potential for the fluoromethyl monomers, and one might expect to reach a point at which the electron-withdrawing power of the substituent is sufficient to inhibit the oxidation of monomer and subsequent formation of a polymer film. Waltman et al.[6] first noted a correlation between monomer oxidation potentials and polymer formation with the Hammett substituent constants for 3-substituted thiophenes. At that time their plot of E_{pa}(mon) vs σ covered a range over which oxidative polymerization occurred and included thiophene, 3-alkylthiophenes, 3-bromothiophene, and 3-iodothiophene. This range would also have included the then-unsynthesized 3-(polyfluoroalkyl)thiophenes and 3-(fluoromethyl)thiophene based on the magnitude of those substituent constants. Only thiophene and the 3-alkylthiophenes were reported to yield high quality polymer films while 3-bromothiophene and 3-iodothiophene yielded only poor-quality films of low conductivity. The preparation of high-quality poly(3-bromothiophene) films has since been reported[7] as well as those of the 3-(polyfluoroalkyl)thiophenes reported by Büchner et al.[3] The plot of Waltman et al.[6] also included the oxidation of 3-thiophene monomers with carboxylic acid, cyano, and nitro substituent groups; however, these derivatives failed to yield polymer films owing to the strong electron-withdrawing power of the substituents. In this work, we report the oxidative polymerization of the 3-(fluoromethyl)thiophenes. This includes 3-(difluoromethyl)thiophene and 3-(trifluoromethyl)thiophene which have Hammett substituent constants significantly greater than those of the 3-(polyfluoroalkyl)thiophenes.

The syntheses of the new compounds 3-(fluoromethyl)-thiophene and 3-(difluoromethyl)thiophene were carried out by the reaction of 3-thiophenemethanol and 3-thiophenecarboxylic acid with DAST in dichloromethane. The use of DAST as a fluorinating reagent is well-known.[8] **Caution!** *DAST reacts violently with water and may*

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Table I. Electrochemical Data[a]

	E_a(mon)	$E°$(poly)	$E_{pa} - E_{pc}$
RCH_3	1.78	0.96	0.09
RCH_2F	2.00	1.33	0.35
$RCHF_2$	2.27	1.43	0.42
RCF_3	(1.92)	(1.16)	(0.53)

[a] In volts vs Ag pseudoreference. R = 3-thienyl.

undergo explosive decomposition at temperatures greater than 60 °C. Gas chromatograms of the crude product mixtures showed high conversion of the starting material to the end product in each case (>90%). Büchner et al.[1] noted a low isolated yield (30%) in their procedure to prepare the difluoromethyl derivative which involved hydrolysis of the reaction mixture with water to terminate the reaction. We also obtained poorer yields when hydrolyzing the reaction with water and have sometimes observed the chemical polymerization of the products resulting in the formation of blue-black solids. Direct vacuum distillation of the reaction mixture to separate the product from unreacted DAST and avoidance of the use of water in the workup gave significantly improved isolated yields. We employed several known routes for the preparation of 3-(trifluoromethyl)thiophene and observed that the copper-mediated reaction of 3-iodothiophene and trifluoromethyl iodide in dimethyl sulfoxide gave the highest yields.[9-12] Our general characterization of 3-substituted thiophenes has been previously reported,[13] and complete data for 3-(fluoromethyl)thiophene and 3-(difluoromethyl)thiophene are given below.

The oxidative polymerization of the 3-(fluoromethyl)-thiophenes has been carried out in $TBAPF_6$/nitrobenzene solutions on either platinum mini-electrodes (Cypress) or indium-doped tin oxide glass (ITO) electrodes (Donnelly). The electrochemical properties of the 3-(fluoromethyl)-thiophene series have been characterized in terms of the potential for the onset of monomer oxidation, E_a(mon), and the redox properties of the resulting polymer, E_{pa}, E_{pc}, and $E°$(poly), Table I. We have included data for 3-methylthiophene[13] as part of the series. Other data for 3-methylthiophene are available in the literature.[14] On a scan to positive potential, each monomer solution gave a rapid increase in current at the electrode and an irreversible oxidation wave characteristic of thiophenes under similar conditions (example in Figure 1). We note that a greater oxidation potential is required as the number of fluorine atoms increases in the series $-CH_3 < -CH_2F < -CHF_2$ until 3-(trifluoromethyl)thiophene which surprisingly was observed to have lower oxidation potential than the difluoromethyl derivative; further work will be necessary to confirm this tentative and unexpected result. The anodic and cathodic waves in the cyclic voltammogram of 3-(fluoromethyl)thiophene were somewhat broad and not well-defined compared to other poly(3-substituted thiophenes) which we have observed.[13] The polymer films were red-orange in the reduced, nonconductive state and slate-green in the oxidized, conductive state and, although the films appeared to be of good quality on the ITO

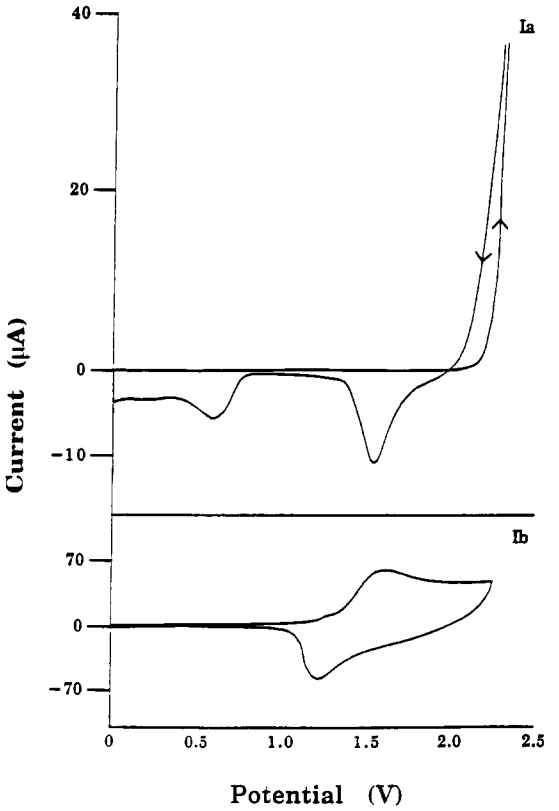

Figure 1. (a) First scan showing nucleation loop and reduction of polymer on Pt electrode for 3-(difluoromethyl)thiophene (0.1 M) in 0.2 M $TBAPF_6$–nitrobenzene at 100 mV s^{-1}. (b) Oxidation and reduction of polymer formed from 3-(difluoromethyl)-thiophene on Pt electrode in 0.2 M $TBAPF_6$–nitrobenzene at 100 mV s^{-1}.

electrode surface, they could only be removed from the electrodes in strips. The polymers prepared from 3-(difluoromethyl)thiophene and 3-(trifluoromethyl)thiophene are red in the reduced state and blue in the oxidized state. Films prepared from 3-(difluoromethyl)thiophene are of high quality and easily removed from the electrode, while the polymer prepared from 3-(trifluoromethyl)thiophene appeared powdery and could not be removed from the electrode as a film. Oxidized poly(3-(fluoromethyl)-thiophene) and poly(3-(difluoromethyl)thiophene) appear to be unstable when exposed to air, water, and selected organic solvents; they undergo a color change which indicates chemical reduction is taking place. This behavior is not observed for either polythiophene or poly(3-methylthiophene) and is consistent with the considerably higher oxidation potentials observed for the 3-(fluoromethyl)thiophenes reported here. This instability is reflected in the low conductivity, measured by the four-point probe method (10^{-5} S cm^{-1}), of a film of oxidized poly(3-(difluoromethyl)thiophene) which apparently becomes partially reduced over the time required to make the measurement. Experiments to measure the conductivity of the films in a rigorously dry and inert atmosphere are underway.

Semiquantitative data obtained from the energy-dispersive X-ray spectra (EDAX) of an oxidized poly(3-(difluoromethyl)thiophene) film indicated a sulfur/phosphorus ratio (as PF_6^-) of 9, indicating an approximate doping level of 11%. The sulfur/fluorine ratio for the oxidized film (0.4) was roughly consistent with the doping level and indicated a poly(3-(difluoromethyl)thiophene) film composed of one PF_6^- for every 12 thiophene units.

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The reduced film was observed to have a sulfur/fluorine ratio of 0.5, consistent with the two fluorine atoms of the difluoromethyl group per sulfur atom, while the sulfur/phosphorus ratio for the reduced film was approximately 30 signifying nearly complete undoping of the polymer.

Visible spectra of the as-grown films of poly(3-(fluoromethyl)thiophene) and poly(3-(difluoromethyl)thiophene) on ITO electrodes have also been obtained. The reduced films of both polymers exhibit a broad absorption band near 440 nm, while the oxidized films show a modest decrease in the intensity of this transition and the appearance of a second transition at a lower energy. The lower energy transition is well defined for poly(3-(difluoromethyl)thiophene) and is limited to the visible region (600–820 nm) with a maximum at 750 nm, while the transition for poly(3-(fluoromethyl)thiophene) is less well defined, is also limited to the visible region, and appears to have a maximum near 610 nm. The high-energy transition observed for the reduced films is indicative of the polymer bandgap transition, while the lower energy transition observed for the oxidized polymers apparently arises from the highest energy polaron transition within the polymer bandgap.[15] We have previously observed the bandgap transition to occur at 480 nm for poly(3-methylthiophene).[13] The higher energy bandgap transition for the fluorinated polymers over poly(3-methylthiophene) is consistent with the higher value of $E°$, whereas the observation of a polaron rather than a bipolaron transition in the visible spectra of the oxidized polymer films is consistent with the observed low doping level of the polymers by EDAX. Each of these results agrees with the lower conductivity of poly(3-difluoromethyl)thiophene) which most probably results from partial reduction of the film during the measurements.

The difference in $E°$ between poly(3-(difluoromethyl)-thiophene) and poly(3-methylthiophene) suggests that the 3-fluoroalkyl polymer could serve as the cathode and the 3-alkyl polymer as the anode of an all-polymer battery. Indeed, when films of each polymer were prepared on ITO electrodes and immersed in $TBAPF_6$/nitrobenzene, and the cell was discharged through a resistor, the blue poly-(3-(difluoromethyl)thiophene) cathode turned red and the red poly(3-methylthiophene) anode turned blue. More quantitative experiments on this system are in progress.

The successful oxidative polymerization of these 3-(fluoromethyl)thiophenes demonstrates that conductive polymers can be prepared from thiophenes with fluorinated side chains directly attached to the thiophene ring. The fact that the redox potentials for these two fluorinated polymers are significantly greater than those for the nonfluorinated alkyl analogs makes these new conductive polymers extremely attractive as electrode materials.

3-(Fluoromethyl)thiophene: isolated yield 55%. Anal. Calcd for C_5H_5FS: C, 51.70; H, 4.34; F, 16.36; S, 27.60; MW, 116.158. Found: C, 51.93; H, 4.43; F, 16.22 (by difference); S, 27.42. ^1H NMR (δ) 7.10–7.16 broad, three lines 1H, H_4; 7.35 d 2H, H_2 and H_5; 5.37 d, $-CH_2F$; (H–H coupling unresolved; $^1J_{H-F}$ 47.9 Hz). ^{13}C NMR (δ) 124.75 d, C_2; 137.30 d, C_3; 127.06 d, C_4; 126.58 s, C_5; 79.54 d, $-CH_2F$; (J_{C2-H2} 185.0 Hz; J_{C4-H4} 169.2 Hz; J_{C5-H5} 186.8 Hz; J_{C-H} ($-CH_2F$), 153.3 Hz; $^1J_{C-F}$ 164.6 Hz; $^2J_{C3-F}$ 19.0 Hz; $^3J_{C2-F}$ 7.9 Hz; $^3J_{C4-F}$ 2.9 Hz). ^{19}F NMR (δ) −203.2 t; ($^1J_{F-H}$ 48.4 Hz). IR (cm^{-1}) 3095 m, 2950 m, 2885 m, 1462 w, 1405 m, 1358 m, 1243 m, 1215 m, 1153 s, 1073 m, 965 vs, 924 m, 852 s, 825 s, 775 vs, 685 vs, 628 m, and 557 m. MS (*m/e*, ion, rel %) 115.10, $C_4H_3SCHF^+$, 100.0; 116.20, $C_4H_3SCH_2F^+$, 82.3; 45.20, CHS^+, 50.0; 97.20, $C_4H_3SCH_2^+$, 39.1; 39.20, $C_3H_3^+$, 12.9; 57.20, C_2HS^+, 12.8; 51.20, $C_4H_3^+$, 10.5; 69.10, $C_3H_2SCF^+$, 9.7; 71.20, $C_3H_2SCH_2F^+$, 5.4; 38.20, $C_3H_2^+$, 5.1; 32.20, CHF^+, 4.5; 70.20, $C_3H_2SCHF^+$, 4.0; 33.20, CH_2F^+, 2.9. UV: λ_{max} = 234 nm, log ϵ = 3.62.

3-(Difluoromethyl)thiophene: isolated yield 73%. Anal. Calcd for $C_5H_4F_2S$: C, 44.77; H, 3.01; F, 28.32: S, 23.90; MW, 134.148. Found: C, 44.74; H, 3.04; F, 28.24 (by difference); S, 23.98. ^1H NMR (δ) 7.56 m, H_2; 7.22 d, H_4; 7.39 m, H_5; 6.71 t, $-CHF_2$; (J_{2-4} 1.41 Hz; J_{2-5} 2.98 Hz; J_{4-5} 5.07 Hz; $^1J_{H-F}$ 56.4 Hz). ^{13}C NMR (δ) 125.18 t, C_2; 136.22 t, C_3; 124.49 t, C_4; 127.18 s, C_5; 111.79 t, $-CHF_2$ (J_{C2-H2} 186.4 Hz; J_{C4-H4} 169.9 Hz; J_{C5-H5} 187.3 Hz; J_{C-H} ($-CHF_2$), 186.4 Hz; $^1J_{C-F}$ 237.0 Hz; $^2J_{C3-F}$ 24.7 Hz; $^3J_{C2-F}$ 7.7 Hz; $^3J_{C4-F}$ 3.6 Hz). ^{19}F NMR (δ) −108.8 d; ($^1J_{F-H}$ 56.5 Hz). IR (cm^{-1}) 3105 w, 2970 w, 1542 w, 1410 s, 1345 s, 1240 m, 1220 w, 1163 s, 1010–1070 vs (br), 860 m, 838 s, 792 vs, 740 vs, 695 m, 645 m, and 552 w. MS (*m/e*, ion, rel %) 134.00, $C_4H_3SCHF_2^+$, 100.0; 133.00, $C_4H_3SCF_2^+$, 98.3; 45.00, CHS^+, 56.1; 115.00, $C_4H_3SCHF^+$, 41.9; 84.00, $C_4H_4S^+$, 41.9; 39.00, $C_3H_3^+$, 26.7; 57.00, C_2HS^+, 11.9; 51.10, $C_4H_3^+$ and CHF_2^+, 11.0; 58.00, $C_2H_2S^+$, 10.7; 50.05, $C_4H_3^+$ and CF_2^+, 6.4; 31.10, CF^+, 6.2; 89.00, $C_3H_2CHF_2^+$, 3.5; 88.00, $C_3H_2CF_2^+$, 3.3. UV: λ_{max} = 231 nm, log ϵ = 3.87.

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