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The preparation and oxidative polymerization of 3-thienylperfluoroacylamides

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Abstract

The previously known 3-thienyltrifluoroacetamide (**1**) and the new compound, 3-thienylheptafluorobutyramide (**2**) have been synthesized in high purity by a new route and characterized by spectroscopy and elemental analysis. Both substances can be electrochemically polymerized to yield electrically conducting films. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

We have been interested in the synthesis and electropolymerization of thiophenes substituted in the 3-position with electron-withdrawing substituents which can raise significantly the onset potentials for oxidation of the monomers and, consequently, can raise the oxidation potentials of the polymers formed from them as well [1–3]. It has been also shown that bis(perfluoroacyl)- [4] and bis(perfluoro-sulfuryl)imides [5] are very acidic and readily dissociate in aqueous solution to the extent that phosphoric acid does (pK_a 2). It became of interest to us to seek to combine these two properties in one thiophene unit which, owing to the incorporation of a labile hydrogen atom on the amide group, might be able to act as a self-doping polymer.

Although this goal was not realized with the title compounds, progress has been made on the synthesis and characterization of this class of substances which may ultimately have applications; our research in this area is continuing. In this work, we report the successful synthesis of (**1**) [6] by a method previously used only for the preparation of the non-fluorinated analogs, the synthesis and characterization of (**2**), and the electropolymerization of these substances.

2. Experimental

2.1. Materials

3-Methylthiophene (99+%), $NH_2OH \cdot HCl$ (99%), $TBAPF_6$ (98%), tetrahydrofuran (anhydrous, 99.9%), $(CF_3C(O))_2O$ (99%), and tetrahydrothiophene-3-one (98%) (Aldrich), $(C_3F_7C(O))_2O$ (99%) (PCR), CH_3CN (99+%) (Fisher), and $CF_3C(O)NH_2$ (Columbia Organic) were used as received except for CH_3CN which was distilled from calcium hydride and $(CF_3C(O))_2O$ which was dried under vacuum prior to use. Other materials used were micropolishing agents (1–0.05 μ α-Al_2O_3) (Buehler), copper wire (0.001 in diameter) (Omega Eng.) and In-doped tin oxide-coated glass (Donnelly).

2.2. Instrumentation and methods

NMR spectra were obtained on a Varian VXR 200 MHz FT-NMR Spectrometer using TMS (^{1}H, ^{13}C) and CCl_3F (^{19}F) as internal references. Other measurements involved use of a HP8452A Diode Array Spectrophotometer (UV–Vis), a Mattson 4020 Galaxy FTIR, and a Phillips 515 SEM with a PV9800 EDAX attachment. Elemental analyses were performed by Atlantic Microlabs. CV and constant potential measurements were performed using an EG and G PARC 173 Potentiostat/Galvanostat with a 179 Digital Coulometer and a 175 Universal Programmer. The polymerizations were carried out in a 10 ml cell using an ITO as working electrode, a Pt flag as counter electrode, and a Ag wire reference electrode [7]; the potential was checked against the Fc/Fc^+ redox couple.

2.3. Thienyltrifluoroacetamide, $C_4H_3SN(H)C(O)CF_3$ (1)

A method reported for the synthesis of 3-thienylacetamides [8] was applied to that of 3-thienylperfluoroacylamides. After $(CF_3CO)_2O$ was added to the reaction mixture [8] at 5°C, the product mixture was brought to 25°C,

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concentrated on a rotary evaporator, and the residue was dried overnight on a vacuum line. The product sublimed as a white solid from a vessel held at 150°C. (**1**) 21%. M.P.: 123.5–124°C. *Anal.* Calc. for C, 36.9; H, 2.07; S, 16.4; N, 7.18; (F,O), 37.4. Found: C, 37.2; H, 2.11; S, 16.2; N, 7.05; (F,O), 37.5. NMR. ^{19}F (Φ, ppm): −75.6 s. ^{1}H and ^{13}C spectra and *J* values were in agreement with those reported for (**1**) prepared by a different method [6]. IR (cm^{-1}): 3280 m, 3145 m, 3120 m, 1700 s, 1595 m, 1540 w, 1385 w, 1325 w, 1190 s, 1155 s, 1140 s, 960 w, 905 w, 865 w, 835 w, 772 s, 680 w, 620 w.

A previous method for the synthesis of 3-thienylacylamides similar to the one above but utilizing $BaCO_3$ [9] instead of a polar solvent [8] gave a yield of only 16%. Other methods involving addition of acyl anhydrides to 3-aminothiophene prepared by reactions of bromothiophenes in liquid ammonia [10] gave even lower yields (5%).

2.4. *3-Thienylheptafluorobutyramide, $C_4H_3SN(H)C(O)C_3F_7$ (**2**)*

3-Aminothiophene [8] was prepared as above, and $(C_3F_7C(O))_2O$ (0.0098 mol) was added to the resulting methylene chloride solution; the mixture was warmed to 25°C with stirring, the solvent was stripped, and the residue was dried overnight under vacuum. The vessel was heated to 150°C under vacuum and a white sublimate was collected. (**2**) 17% M.P. 106–107°C. *Anal.* Calc. for C, 32.56; H, 1.37; S, 10.87; N, 4.75; (F, O), 50.45. Found: C, 32.37; H, 1.40; S, 10.51; N, 4.75; (F, O), 50.97. NMR (δ, ppm; *J*, Hz): ^{1}H. 8.24 b (NH); 7.68 dd (H_2); 7.31 dd (H_5); 7.08 dd (H_4); $J_{24} = 1.41$; $J_{25} = 3.23$; $J_{45} = 5.25$. ^{13}C. 133.2 s (C_3), 126.1 s (C_5), 121.4 s (C_4), 113.9 s (C_2), 155.1 t (CO), (CF_x) region unresolved due to ^{19}F coupling. ^{19}F (Φ). −80.58 t (F^{γ}), −120.1 q (F^{α}), −126.6 m (F^{β}); $J_{\alpha-\gamma}$=8.85, $J_{\alpha-\beta/\gamma-\beta}$ <1. IR (cm^{-1}): 3310 m, 3140, 3100 w, 1690, 1570, 1535 s, 1410 w, 1370 w, 1345 w, 1285 w, 1225 m, 1200 s, 1180 m, 1130, 1110 s, 960 w, 945 w, 875 w, 840 w, 820 w, 770 m, 750 w, 675 w, 605 m. When an earlier procedure [9] was applied, yields were consistently lower (12%).

2.5. *Oxidative polymerization Of (**1**) and (**2**)*

For the CV measurements, the usual precautions with regard to oxygen and water were taken, and a flat base line was established for a blank (0.1–0.2 M $TBAPF_6/CH_2Cl_2$) after which monomer was added (0.03–0.05 M). The working electrode was then cycled once between 0.0 and 1.30 V; after each scan, the potential upper limit was increased incrementally by 50–100 mV and another scan was carried out. The incremental steps were discontinued when nucleation occurred and growth of polymer on the ITO electrode began. The system was allowed to cycle at this potential range until polymer completely covered the electrode. The film was washed several times with fresh CH_2Cl_2 and dried before analysis by SEM and EDAX.

For preparative scale samples, a constant potential (2.0 V), set higher than the onset potentials (1.63 for (**1**), 1.93 for (**2**)) to ensure a sufficient polymerization rate, was applied to the working electrode, and the experiment was terminated after a fixed charge had passed. A sample of the film prepared from (**1**), cleaned as above, gave the following analytical results. Found: C, 32.20; H, 2.29; N, 6.09; S, 13.68, (F, O, P), 45.74. $\{(C_4HSN(H)C(O)CF_3)_9^{2+}2PF_6^-\}_n$ requires C, 32.00; H, 0.99; N, 6.22; S, 14.23, (F, O, P), 46.72. EDAX measurements were consistent with this finding. Conductivity measurements were made by attaching a sample of dry film (1.5 × 0.75 cm^2) with no breaks or fractures to a four-point probe constructed in our laboratory after van der Pauw [11]. The current/potential data gave conductivities of 4.4×10^{-3} (**1**) and 1.7×10^{-3} S cm^{-1} (**2**). Polypyrrole was determined to have a conductivity of 32 S cm^{-1} consistent with the values previously measured in our laboratory [12].

3. Results and discussion

Alteration of the monomer structure by addition of substituents in the 3-position of the ring can change the electronic and electrochemical properties of the polymer. It has been shown that poly(heterocycles) with less 2,3′-defects and more 2,5-links generally have higher conductivities and better electronic properties; blocking the 3-position favors 2,5-linkage. The strategy was also to employ highly electron-withdrawing substituents to lower the energy of the π-HOMO [13,14] and, consequently, raise the oxidation potential of the monomer. This, in turn, would produce a polymer which would be strongly oxidizing and which could be useful as an anode material in a battery. We chose to investigate two 3-thienylperfluoroacylamides since the electron-withdrawing perfluoroacyl group would render the nitrogen atom more positive thereby increasing the acidity of the proton which might possibly confer a self-doping property on the polymer. Thus, the diffusing species would be a proton which might enhance the rate of the electrochromic effect. Although the oxidation potentials for the monomers are higher than for those bearing electron-donating groups, they are not as high as those for which the electron-withdrawing substituent is directly attached to the ring nor is there any evidence in these two cases that the rate of electrochromism is enhanced for thick films.

3.1. *Synthesis and characterization*

A number of methods for the synthesis of 3-aminothiophene, the precursor to (**1**) and (**2**), has been reported [8–10,15–19]. Of these, all of which were tried, the method described by Barker [8] proved best. (**1**) has been prepared previously by a different method [6] but (**2**) has not. In all cases, the yields for (**1**) and (**2**) were lower than those for non-fluorinated species [20]. The elemental analyses established a high level of purity for (**1**) and (**2**) prepared by the preferred method. The ^1H, ^{19}F, and ^{13}C NMR spectra support the proposed structures of both compounds. The NH proton appears as a broad resonance near 8.2 ppm, and the three aromatic protons on the thiophene ring can be seen as doublets of doublets between 7.0 and 7.8 ppm. Further evidence for the assignments was obtained from a 2D heteronuclear correlated spectrum for carbon and hydrogen which indicated that the order in the downfield direction is H_4, H_5 and H_2. The ^{19}F NMR spectrum shows a singlet for the CF_3 group in (**1**) and three resonances for the α-CF_2, β-CF_2, and γ-CF_3 fluorine atoms in (**2**). These assignments are consistent with those in the literature [21] for thiophenes and the ^1H spectrum of (**1**) [6]. The N–H stretching vibration appears at 3300 and 3320 cm^{-1} for (**1**) and (**2**), respectively, and the C–H ring-stretching vibrations are a closely spaced doublet between 3100 and 3150 cm^{-1}. The carbonyl stretch is observed at 1700 cm^{-1} for both the compounds. Thiophene ring bands between 1600 and 1500 cm^{-1} presumably due to C–C and C–S stretching are also observable [22]. Bands in the range of 1100–1400 cm^{-1} are assigned to C–F stretching vibrations, and finally a hydrogen out-of-plane stretch is observed at 770 cm^{-1} for both substances. This band is unique to 3-substituted thiophenes and has proved to be reliable in distinguishing between 2- and 3-substitution [23].

3.2. Oxidative polymerization

Fig. 1 shows several potential sweeps (8,10,13,14,15 and 16, respectively), which demonstrate the growth of a polymer film from (**1**) on a platinum electrode. The initial potential range was 0.0–1.0 V. After each scan the anodic potential was increased, in this case, by a 100 mV increment (E_{onset}, 1.7 V); above 1.7 V, the current increased for each increment until nucleation occurred at 1.9 V as indicated by a cross-over on the cathodic leg of the cycle. Reduction of the resulting polymer can be observed beginning near 0.93 V. After several consecutive scans, both the oxidation and reduction peaks for the polymer are easily observable. The scan in Fig. 1(E) shows a small extra peak on the reverse scan at 0.93 V which may be due to structural reorganization of the film upon oxidation and reduction or distinct differences in the oxidation stages. Such explanations have been given to account for the two cathodic peaks observed for other poly(thiophenes) [14]. The scan in Fig. 1(F) shows the redox process for the polymer film which formed on the surface of the electrode.

Electropolymerization on an ITO electrode results in the reduction peak of the polymer being shifted over time to a more negative potential by 0.36 V for (**1**) and by 0.12 V for (**2**) probably owing to increased resistivity of the films. A second reduction peak can be observed in the voltammogram of (**1**) at about 0.84 V as before. Both polymers of (**1**) and (**2**) show electrochromic behavior (blue/black, oxidized; red/orange, reduced). As the film thickness increased, the color change occurred more slowly owing to the increase in the time for diffusion of the electrolyte into and from the film; this process occurred more slowly for the reduction since anions must diffuse from the film and took several seconds for thick films. These results indicate that the presence of labile hydrogen in the polymer does not enhance the rate of the electrochromic effect.

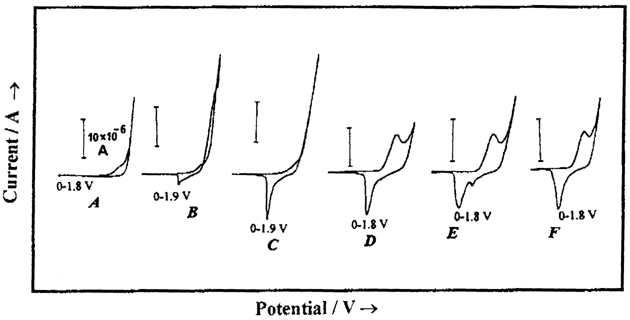

Fig. 1. Cylic voltammograms. 3-thienytrifluoroacetylamide. A, cycle 8; B, cycle 10; C, cycle 13; D, cycle 14; E, cycle 15; F, cycle 16. WE, Pt, $r = 5 \times 10^{-4}$ m; CE, Pt flag; RE, Ag wire; 3-thienyltrifluoroacetylamide, 0.03 M; $TBAF_6/CH_2Cl_2$, 0.1 M; $v = 0.1$ V s^{-1}.

Preparative scale synthesis of the polymers was carried out by constant potential electrolysis. The potential for polymerization was determined by first setting it to that for the onset of oxidation of the monomer. If nucleation did not occur, the potential was increased by 10 mV for 5 min. The potential was incremented until nucleation did occur (1.93–2.0 V for both monomers). When this potential (2.0 V) was applied, the current rapidly increased from 0 μA and a blue conductive film grew on the electrode surface; the run was terminated when a current plateau was reached (2–5 mA cm^{-2}). The electrolyte and monomer concentrations had an effect on the rate of polymerization over a period of time as indicated by the slope of the current/time curve (1.67–8.33 μA s^{-1}). A solution of $TBA^+PF_6^-$ (0.1 M) and monomer (0.03 M) in CH_2Cl_2 gave the highest initial electropolymerization rate, but as the thickness of the film increased, the rate of the electrochemical process slowed (after 10 min. to 0.5 μA s^{-1}) due to increased resistivity. Samples containing trace amounts of water would not nucleate at 2.0 V but would at higher potential at which overoxidation of the film is likely. Completely dry solutions gave the highest rates of polymer production and films having the highest conductivities and strengths.

Scanning electron micrographs of samples of poly-(**1**) and poly-(**2**) show globular features which are typical for poly(thiophenes) and are consistent with a hemispherical 3D growth pattern from nuclei on the electrode surface (Fig. 2). All surfaces observed at different magnifications were rough compared with those of more conventional poly(thiophenes) [24] and these surface features are in accordance with the low conductivities measured for poly-(**1**) and poly-(**2**). EDAX measurements on both films showed the presence of C, O, F, and P. Nitrogen was detected but was obscured by the intense O and C peaks

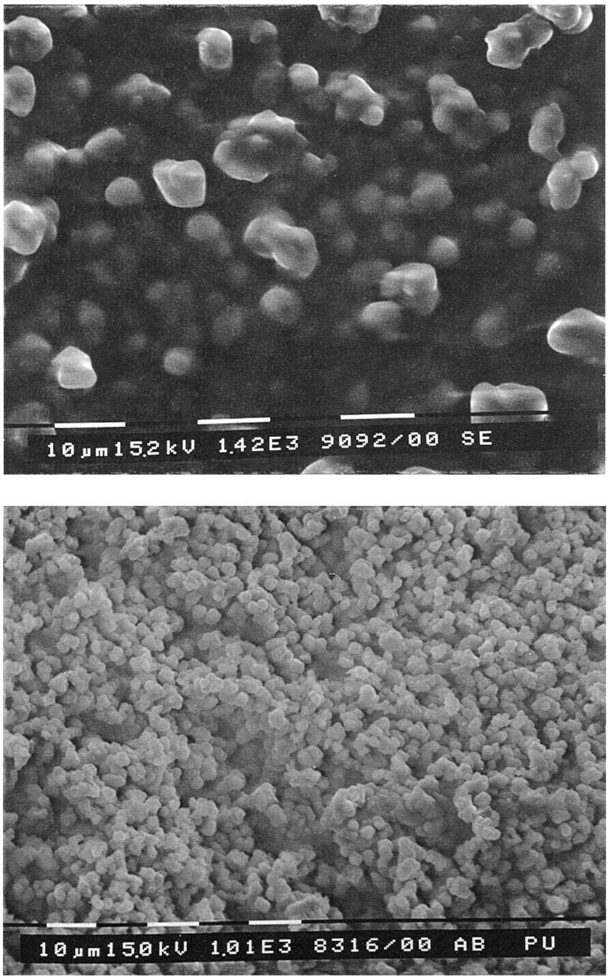

Fig. 2. Scanning Electron Micrographs. Top: 3-thienyltrifluoroacetylamide 1400X magnification. Bottom: 3-thienylheptafluorobutyrylamide, 1000X magnification.

which were very closely spaced. The presence of phosphorus indicates that there is a level of doping in the polymer consistent with the measured conductivity. In further support of this, Pd coating of the film was unnecessary to obtain SEM data.

Specular reflectance IR spectra of poly-(**1**) and poly-(**2**) exhibit an N–H stretching mode close to 3200 cm^{-1}, a carbonyl stretching mode near 1700 cm^{-1}, and C–F stretching vibrations between 1400 and 1100 cm^{-1}. These results indicate that the ring structure and side-chain of the monomer are intact after polymerization. An intense band arising in the visible region and extending over the near IR region is observed which is indicative of polaron and bipolaron formation in the doped polymer [25].

An elemental analysis of poly-(**1**), coupled with EDAX measurements, was in rough agreement with the composition $\{[C_4HSN(H)C(O)CF_3]_9{}^{2+} \cdot 2PF_6{}^-\}_n$ which suggested that there were about nine thiophene units per two electrolyte anions. However, the polymer does not stay in the oxidized state under ambient conditions for any length of time as indicated by a color change. The conductivities for these thiophene polymers are low which is consistent with this observation (10^{-3} S cm^{-1}) but of the same order of magnitude as those of poly(3-alkoxythiophenes) although poly(3-alkylthiophenes) have conductivities as high as 200 S cm^{-1} [3]. Attempts to optimize the conductivity of these materials have not been made yet and it is possible this will result in considerable improvement. We are continuing work in this area.

4. Conclusions

(**1**) [6] and the new compound, (**2**), were synthesized by a method not previously employed for the preparation of 3-thienylperfluoroacylamides. The successful synthesis of the latter substance suggests that a series of 3-thienylperfluoroacylamides would be possible by the reaction of a variety of perfluoroacyl anhydrides with the unstable 3-aminothiophene intermediate. (**1**) and (**2**) can be polymerized by electrochemical oxidation to form thin, free-standing, conductive polymer films which exhibit electrochromism and have conductivities in the range of 1×10^{-3} to 5×10^{-3} S cm^{-1}. The films produced were not stable in the atmosphere and spontaneously reduced to their neutral form indicating that they are oxidizing. Under the conditions in which they were produced, the films were brittle and non-flexible.

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References

[1] R.J. Waltman, J. Bargon, Can. J. Chem. 64 (1986) 76.
[2] S.K. Ritter, R.E. Noftle, Chem. Mater. 5 (1993) 752.
[3] S.K. Ritter, R.E. Noftle, Chem. Mater. 4 (1992) 872.
[4] P.M. Narula, M.A. Odian, B.A. Powers, A. Lachgar, W.T. Pennington, R.E. Noftle, Thirteenth Winter Fluorine Conf., 19–24 January 1997, St. Petersburg, FL.
[5] J. Foropoulos, D.D. DesMarteau, Inorg. Chem. 23 (1984) 3720.
[6] M. Prats, C. Galvez, Heterocycles 34 (1992) 149.
[7] R.A. Malmsten, C.P. Smith, H.S. White, J. Electroanal. Chem. 215 (1986) 223.
[8] J.M. Barker, European Patent No. 0 298 542, A1. 1989.
[9] M. Murakami, M. Hikichi, Japanese Patent No. 69,12,895, Chem Abstr. 1969, 71, 101702b.
[10] M.G. Reinecke, H.W. Adickes, C. Pyun, J. Org. Chem. 36 (1971) 2690.
[11] L.J. van der Pauw, Philips Res. Rep. 13 (1958) 1.
[12] Wu, Y., M.S. Thesis, Wake Forest University, 1989.
[13] J. Roncali, Chem. Rev. 92 (1992) 711.
[14] J. Heinze, in: E. Steckhan (Ed.), Topics in Current Chemistry: Electrochemistry IV, Springer, Berlin, vol. 151, Ch. 1, 1990.

[15] E. Campaigne, P.A. Monroe, J. Am. Chem. Soc. 76 (1954) 2447.
[16] E.W. Brunett, D.M. Altwein, W.C. McCarthy, Heterocyclic Amines 6 (1973) 1067.
[17] R.K. Norris, in: S. Gronowitz (Ed.), Heterocyclic Compounds, Wiley, New York, vol. 44, Part II, 1985, p. 638.
[18] R.A. Hoffman, S. Gronowitz, Arkiv. Kemi 16 (1961) 515.
[19] W. Steinkopf, T. Hopner, Ann. Chem. 501 (1933) 174.
[20] H.C. van der Plas, D.A. de Bie, G. Geurtsen, M.G. Reinecke, H.W. Adickes, Rec. Trav. Chim. 93 (1974) 33.
[21] S. Gronowitz, A. Hornfeldt, in: S. Gronowitz (Ed.), The Chemistry of Heterocyclic Compounds, Wiley, New York, vol. 44, Part 4, Ch. 1, 1984.
[22] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, 4th ed., Wiley, New York, Ch. 3, 1983.
[23] S. Gronowitz, R. Hakansson, Arkiv. Kemi 16 (1960) 309.
[24] Z. Qi, P.G. Pickup, J. Electroanal. Chem. 335 (1993) 133.
[25] A. Ivaska, M. Kaponen, P. Passimilmi, L.E. Osterholm, Synth. Metals 28 (1989) C859.