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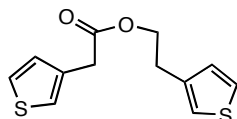
SYNTHESIS AND ELECTROPOLYMERIZATION OF 2-(3-THIENYL-ETHYL)-3-THIOPHENEACETATE (1)

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Introduction

Conducting polymers offer great promise in the development of electronic devices, displays and sensors. In that regard, biomolecules can be attached to these polymers via functional groups, but the presence of such groups oftentimes hinders polymerization.¹⁻³ One strategy is to polymerize a functionalized monomer precursor of a conducting polymer, followed by reaction of the dangling functional groups of the polymer with appropriately functionalized labels. An attractive functionalized thiophene for that purpose is 3-thiophenylethanol. Unfortunately, however, this monomer is not polymerizable.^{1,2} Thus, 3-thiophenylethanol has been esterified, followed by co-polymerization with 3-methylthiophene (3-MT), and subsequent hydrolysis of the ester to the free alcohol.^{1,2} Here, we present a viable alternative, whereas we have synthesized monomer **1** from commercially



available 3-thiopheneacetic acid and 2-(3-thiophenylethanol). Monomer **1** was electropolymerized both by itself and as a copolymer with 3-methylthiophene (3-MT). The ester linkage was reduced with LiAlH₄, and the resulting hydroxyl groups were re-esterified by reaction with acetyl chloride. The functional group transformations were followed by FT-IR.

Experimental

Materials. All reagents and solvents were used as received unless otherwise noted. Anhydrous acetonitrile, 3-methylthiophene (3-MT), 3-thiopheneacetic acid (98%), 2-(3-thiophenylethanol) (99%), and thionyl chloride (97%) were purchased from Aldrich Chemical Co. Triethylamine was purchased from Acros Chemicals and was further purified by distillation from calcium hydride. Tetrabutylammonium perchlorate (TBAP) was prepared from an aqueous solution of tetrabutylammonium bromide (Aldrich) and 70% aqueous HClO₄ as described before.

Synthesis of 1. A solution of 3-thiopheneacetic acid 5.16 g (~0.0354 mol) in thionyl chloride (16 ml) was refluxed for 1.5 h while protected from moisture with a drying tube. Excess thionyl chloride was removed under reduced pressure and the residue was dried for 3-4 hrs in a vacuum oven (~40 °C) to remove traces of remaining thionyl chloride. To the residue in anhydrous CH₂Cl₂ (44 ml) was added 2-(3-thiophenylethanol) (4 ml, 0.0354 mol) followed by Et₃N 4.9 ml, 0.0354 mol and the reaction mixture was stirred at room temperature for 24 h. It was then extracted with water (3 × 40 ml). The organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified on silica gel column using CH₂Cl₂/1% MeOH as eluent. Further purification by vacuum distillation, gave a pale yellow liquid; b.p. 141-152°C at 0.25 torr; yield: 6.8147g (76.28%). The product was characterized by elemental analysis, ¹³C and ¹H NMR.

Instrumentation and Methods. All electrochemical experiments were conducted using an EG&G 263A potentiostat controlled by the EG&G model 270/250 Research Electrochemistry Software 4.30. Au and Pt disk working electrodes (1.6 mm diameter, 0.0201 cm²) and Ag/AgCl/aqueous KCl (3M) reference electrodes were purchased from Bioanalytical Systems, Inc. (BAS). A Pt mesh was used as a counter electrode. Working electrodes were polished successively with 6, 3, and 1 μm diamond paste (Struers Inc., Westlake, OH), washed with water and acetone, and air-dried. Au coated glass slides were used as working electrodes for FTIR purposes. All volumetric glassware was rinsed with acetone, then water, then soaked in a Micro cleaning solution in water, rinsed with copious amounts of water, and oven dried overnight.

FTIR spectra were recorded on Nicolet Nexus 470 spectrophotometer. Grazing angle studies were performed at 80° using a specular reflectance attachment Model 500 (Thermo Electron Co.).

Electropolymerization and Functional group modification.

Electropolymerization of **1** (0.2 M) was performed voltammetrically at 100 mV/s from a CH₃CN/0.5 M TBAP solution. The return potential, 1.75 V vs. aq. Ag/AgCl, was optimized for maximum film thickness and minimum over-oxidation. Multiple scans were performed on Au-coated glass slides.

Copolymerization was performed at 2:1 mol ratio of **1** (0.2 M) and 3-MT (0.1 M) in anhydrous CH₃CN/0.5M TBAP. The potential scan was from 0 to 1.8 V vs. aq. Ag/AgCl at 100 mV/s.

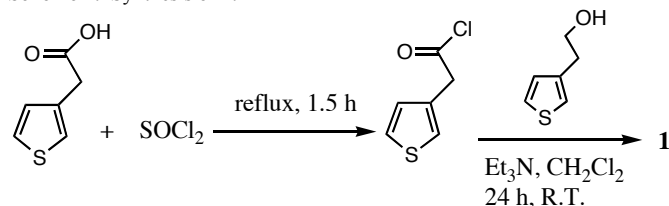
Such polymer films on electrodes were characterized electrochemically in anhydrous CH₃CN/0.1 M TBAP solutions and by FT-IR on Cr/Au-sputter coated glass slides.

Electrodes derivatized with **poly(1)** and **copoly(1)** were first rinsed with acetonitrile, then THF, then with dry THF, then with LiAlH₄ (0.15 g in 10 ml) of dry THF, then with THF, then with isopropyl alcohol/H₂O (9:1, v/v), and finally with THF to give **poly(2)**. These films were again characterized electrochemically and by FT-IR. Such films containing hydroxyl groups were rinsed with CH₃CN and then treated with 1.0 M acetyl chloride in CH₃CN for 15 min to give **poly(3)**. Subsequently, they were rinsed well with CH₃CN and characterized electrochemically and by FT-IR.

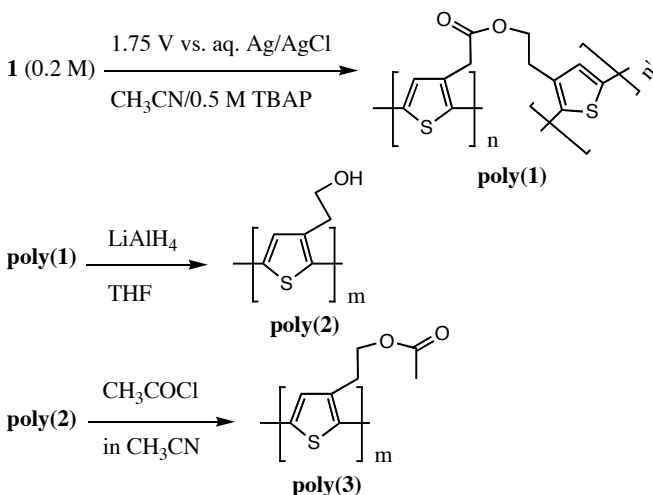
Results and Discussion

Scheme 1 summarizes the synthesis of **1**. Scheme 2 summarizes the electropolymerization, reduction and re-esterification of the reduced hydroxyl groups. Films of **poly(1)** were deposited as described in the experimental section. Figure 1a shows the deposition potential sweep. Figure 1b shows the characterization of **poly(1)** in a fresh solution of CH₃CN/0.1 M TBAP (no monomer). Figures 1c and 1d show the voltammograms of **poly(2)** and **poly(3)** in the same electrolytic solution. The voltammograms of **poly(1)**, **poly(2)** and **poly(3)** are practically identical, although Figure 2 confirms that after treatment with LiAlH₄, the carbonyl peak at 1739 cm⁻¹ is lost, while the -OH absorption at ~3400 cm⁻¹ becomes prevalent (see **poly(2)** spectrum). Subsequent treatment with acetyl chloride, greatly diminishes the intensity of the -OH stretch, while the carbonyl stretch (at 1741 cm⁻¹) reappears.

Scheme 1. Synthesis of 1.



Scheme 2. Electropolymerization of 1, followed by reduction and conversion into an acetyl ester.



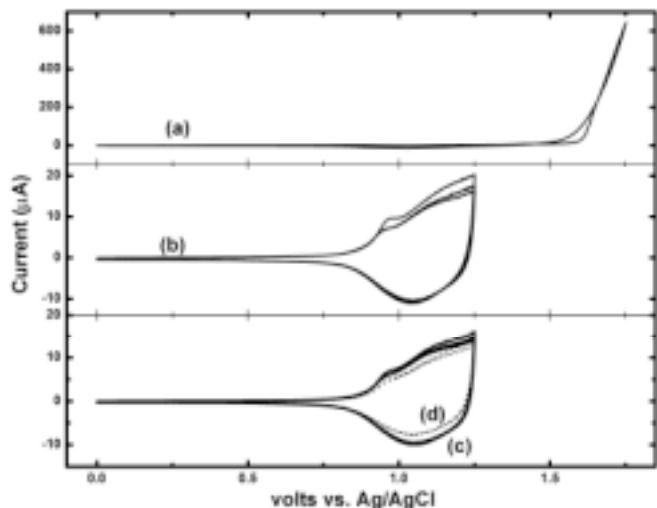


Figure 1. Cyclic voltammetry (CV) on Au electrode (2.1 mm diameter) at 100 mV/s. (a) potential sweep (1 scan) from 0 to 1.75 V vs. aq. Ag/AgCl in a 0.2 M solution of **1** in CH₃CN/0.5M TBAP; (b), (c), (d) CV characterization of **poly(1)**, **poly(2)**, **poly(3)** in CH₃CN/0.1 M TBAP, respectively.

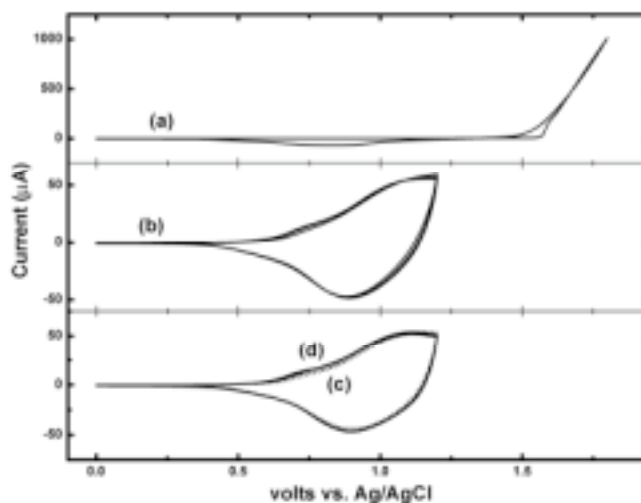


Figure 3. Cyclic voltammetry (CV) on Pt electrode (1.6 mm dia.) at 100 mV/s. (a) potential sweep (1 scan) of **1** (0.2 M) and 3-MT (0.1 M) in CH₃CN/0.5 M TBAP; (b), (c), (d) CV characterization of **copoly(1)**, **copoly(2)**, **copoly(3)** in CH₃CN/0.1M TBAP, respectively.

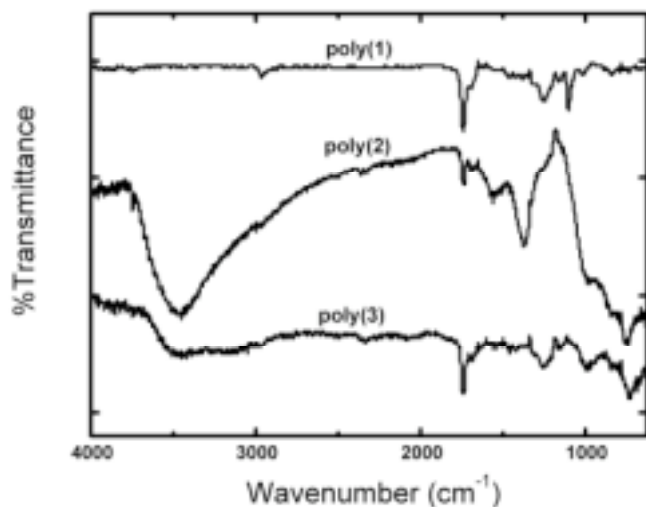


Figure 2. FT-IR spectra of **poly(1)**, the homopolymer of **1**; **poly(2)**, after a 10 sec reaction of **poly(1)** with LiAlH₄ (0.15 g in 10 ml THF); **poly(3)**, after 15 min reaction of **poly(2)** with 1.0 M acetyl chloride in CH₃CN.

Copolymerization of **1** with 3-methylthiophene and subsequent electrochemical characterization of the electrodes shows the same general features as the homopolymer of **1**, although at less positive potentials. Similarly, FT-IR characterization shows that treatment with LiAlH₄ reduces the ester into an alcohol, and subsequent treatment with CH₃COCl regenerates an ester.

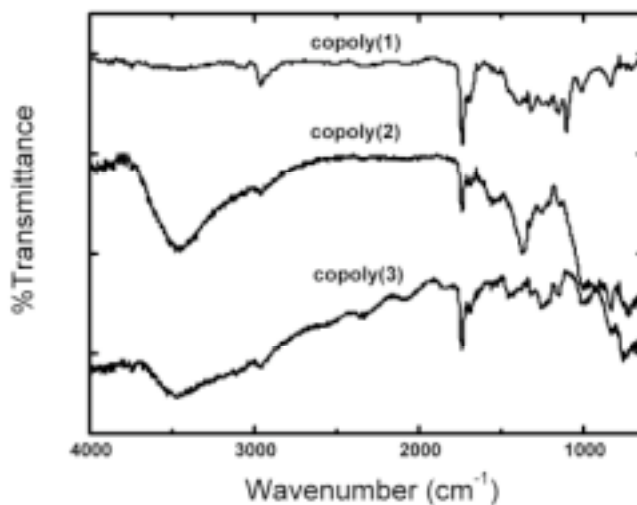


Figure 4. FT-IR spectra of **copoly(1)**, the copolymer of **1** and 3-MT; **copoly(2)**, after 10 sec reaction of **copoly(1)** with LiAlH₄ (0.15 g in 10ml of dry THF); **copoly(3)**, after 15 min reaction of **copoly(2)** with 1.0 M acetyl chloride in CH₃CN.

Conclusions

Monomer **1** can be electropolymerized by itself into durable films, which can be reduced with LiAlH₄ effectively into films of poly[2-(3-thienylethanol)], which can be esterified again with activated carboxylic acids. This reaction is currently explored in our labs for modification of polythiophene films with biomolecules.

References

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