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Reactive Groups on Polymer-Covered Electrodes. 2. Functionalized Thiophene Polymers by Electrochemical Polymerization and Their Application as Polymeric Reagents

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ABSTRACT: Esterification and the consequent reduction of thiophene-3-acetic acid by lithium aluminum hydride produces 3-(2-hydroxyethyl)thiophene (**2**), which must be protected before anodic polymerization. Substance **2** and the protected compounds **3**, **4**, and **5** were investigated by multisweep cyclic voltammetry and characterized by their peak potentials. The poly[3-(2-methoxyethyl)thiophene] (**6**) prepared from 0.05 M monomer solution in acetonitrile by electrochemical polymerization via cyclic voltammetry (ΔE = 0−1.9 V [Ag/AgCl]) is the only electrically conducting polymer. Ether cleavage is carried out in the polymer film **6**, and the resulting poly[3-(2-hydroxyethyl)thiophene] (**7**) reacts with various reagents. The obtained polymer derivatives are characterized by IR reflectance spectroscopy and by electrochemical methods. Polymer **7** is activated with cyanogen bromide to immobilize alcohol dehydrogenase at the surface of the electrode. It was found that the peak potentials of each polymer are characteristic for the appropriate polymer structures.

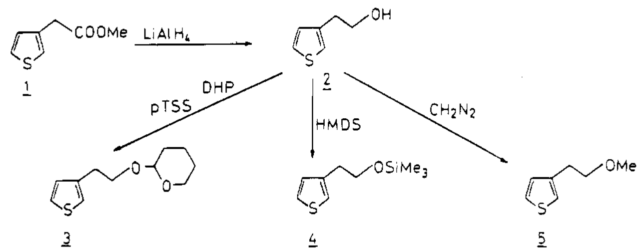
1. Introduction

Heterocyclic compounds such as derivatives of furan and thiophene may be polymerized by specific chemical methods[1,2] and via electrochemical synthesis, e.g., cyclic voltammetry.[3−5] The advantage of electrochemical polymerization lies in the formation of strong adhering polymer films on the surface of metal anodes. Suitable functionalized monomers produce polymers with reactive groups capable of immobilizing reagents. The polymer films have a reasonably high solid-state order and show good electrical conductivities.[6] Therefore it should be possible to apply them in the formation of enzyme electrodes.[7,8]

Reactions with polymeric reagents are fashionable methods now employed for synthesizing in the heterogeneous phase which can be applied in many ways.[9] Approximately 80% of the polymer supporting materials are based on polystyrene.[10] Several publications describe the polymerization of thiophene derivatives[5,11] which are substituted in position 3 and may be assigned for the conversion of the resulting polymers. This paper presents a new method of synthesizing polymeric thiophene derivatives on the electrode surface via electropolymerization and the subsequent conversion to special polymeric materials. The new materials may be employed in a variety of applications, e.g., nonlinear optical polymers and immobilized enzymes for sensor systems.

Methyl thiophene-3-acetate (**1**), available from the corresponding acid, is reduced to give 3-(2-hydroxyethyl)thiophene (**2**). Before the onset of polymerization, the free hydroxy group is protected by three different protecting groups, as shown in Scheme 1 (**3**, **4**, and **5**). Electrochemical polymerization of these substances is carried out in order to obtain thin polymer films with a protected OH group which can be converted to become reactive for film modification.

Scheme 1



2. Experimental Section

2.1. Analytical Methods. The ^{1}H NMR spectra were recorded on a Bruker AM 270. Chemical shifts are expressed in δ relative to tetramethylsilane as internal standard. IR spectra were recorded for films of the appropriate materials using a Perkin-Elmer 580B with a PE 360 data station. Reflection IR spectra on metal surfaces were recorded by a Nicolet 800 FTIR spectrometer. MS data were obtained on a Finnigan MAT 112 and a Finnigan MAT 711. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Thin-layer chromatography was carried out with TLC aluminum sheets precoated with silica gel 60 F_{254}. Thiophene derivatives were identified by an acid solution of isatine, and other substances by development in an iodine atmosphere. Refractive indices were measured on a Carl-Zeiss refractometer.

2.2. Synthesis of the Monomers. Methyl Thiophene-3-acetate (1). Thiophene-3-acetic acid (1.42 g (10 mmol) was dissolved in 20 mL of absolute methanol and 50 mL of chloroform. *p*-Toluenesulfonic acid (0.2 g) was added, and the mixture was refluxed in a Soxhlet apparatus filled with dry sodium sulfate. After the disappearance of the thiophene-3-acetic acid (determined by thin-layer chromatography), the reaction mixture was washed with sodium hydrogen carbonate solution, dried over anhydrous sodium sulfate, and concentrated in vacuo. The resulting dark colored oil was purified by column chromatography (100 g of silica gel 60 (Merck), chloroform). Colorless oil. Yield: 1.43 g (92%). n_D^{20}: 1.5220 (lit.:[12] 1.5243).

3-(2-Hydroxyethyl)thiophene (2). (A) Reduction by Diisobutylaluminum Hydride (DiBAH). Methyl thiophene-

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3-acetate (**1**) (0.80 g (5 mmol)) was dissolved in 5 mL of dry toluene and the mixture was cooled to −78 °C under argon. A 1 M solution of diisobutylaluminum hydride (15 mL (15 mmol)) in toluene was added slowly, the mixture was stirred for 3 h at −78 °C and for 12 h at room temperature. The mixture was then again cooled to −78 °C, and the excess of DiBAH was quenched with 3 mL of methanol. The reaction mixture was then stirred with 20 mL of saturated sodium chloride solution at room temperature and the residue extracted 10 times with 10 mL of ether. The collected ether extracts were dried over magnesium sulfate and concentrated in vacuo. Colorless oil. Yield: 0.61 g (94%).

(B) Reduction by Lithium Aluminum Hydride. Lithium aluminum hydride (0.50 g (13 mmol)) was suspended in dry ether, and the mixture was refluxed for 10 min under argon. After the mixture was cooled to 0 °C, 1.56 g (10 mmol) of **1** was dissolved in 2 mL of dry ether and added to the suspension which was stirred for 1 h at 0 °C. The reaction was quenched with 5 mL of water, the mixture filtered over a G3 frit, and the residue extracted 5 times with ether. The combined organic extracts were dried with magnesium sulfate and concentrated under reduced pressure. Colorless oil. Yield: 1.12 g (88%).

The resulting raw materials may be either employed for following reactions or purified by chromatography (silica gel 60 (Merck), chloroform). n_D^{20}: 1.5508 (lit.:[13] 1.5520).

3-(2-(Tetrahydropyranyloxy)ethyl)thiophene (3). **2** (0.64 g (5 mmol)) was dissolved in 10 mL of dry ether and 10 mL (110 mmol) of freshly distilled dihydropyran. Approximately 200 mg of *p*-toluenesulfonic acid was added and the mixture stirred for 2 days at room temperature. The resulting brown solution was washed with 10 mL of saturated sodium hydrogen carbonate solution, and the organic phase was dried over magnesium sulfate and concentrated in vacuo. The resulting crude dark brown oil (8.20 g) was purified by chromatography (250 g of silica gel 60 (Merck), chloroform). Pale yellow oil. Yield: 0.40 g (71%). n_D^{20}: 1.4462. IR (film): 3101 ($\nu_{C-H\ arom}$); 2940, 2868 ($\nu_{CH\ aliph}$); 1031 cm^{-1} $\nu_{CO\ THP}$). ^{1}H NMR (CDCl$_3$, 270 MHz) (selected signals) δ = 1.27−1.91 (m; 2H, CH$_2$-THP), 2.91 (t; 7 Hz, 2H, thiophene-CH$_2$), 4.61 (m; 1H, OCHO), 7.01 (m; 2H, thiophene), 7.25 (m; 1H, thiophene). MS (80 eV): 212 (M)$^+$ (1.9), 213 (M + 1)$^+$ (0.3), 139 (C_7H_7OS)$^+$ (0.9), 128 ((M + H) − THP)$^+$ (2.1), 111 (M − THP − OH)$^+$ (35), 97 (C_5H_5S)$^+$ (18), 85 (C_4H_5S)$^+$ (100). Anal. Calcd for $C_{12}H_{16}O_2S$ (212.3): C, 62.23; H, 7.60. Found: C, 62.10; H, 7.25.

3-(2-((Trimethylsilyl)oxy)ethyl)thiophene (4). **2** (0.56 g (4.4 mmol)) was dissolved in 10 mL of hexamethyldisilazane (HMDS) and heated at 120 °C for 5 h. After 2 days of stirring at room temperature, the HMDS excess was separated by distillation and the residue purified by chromatography (50 g of silca gel 60 (Merck), chloroform). Colorless oil. Yield: 0.55 g (71%). n_D^{20}: 1.5446. IR (film): 3103 ($\nu_{C-H\ arom}$); 2948, 2875 ($\nu_{C-H\ aliph}$), 1047 cm^{-1} (ν_{C-O-Si}). ^{1}H NMR (CDCl$_3$, 270 MHz): δ = 1.01 (s; 9H, SiMe$_3$), 2.83 (t; 7 Hz, 2H, thiophene-CH$_2$), 3.84 (t; 7 Hz, 2H, CH$_2$O), 6.94 (m; 2H, thiophene), 7.21 (m; 1H, thiophene). MS (80 eV): 200 (M)$^+$ (11), 201 (M + 1)$^+$ (1.8), 185 (M − CH$_3$)$^+$ (24), 128 ((M + H) − SiMe$_3$)$^+$ (35), 111 (M − SiMe$_3$ − OH)$^+$ (14), 97 (C_5H_5S)$^+$ (100). Anal. Calcd for $C_9H_{16}OSi$ (200.4): C, 53.94; H, 8.08. Found: C, 54.23; H, 7.71.

3-(2-Methoxyethyl)thiophene (5). **2** (0.56 g (4.4 mmol)) was dissolved in 10 mL of dry ether containing three drops of boron trifluoride diethyl ether complex. Then 20 mL (ca. 20 mmol) of a diazomethane solution in ether was added carefully under violent effervescence. The reaction solution was stirred for 1 h at room temperature, filtered, concentrated in vacuo, and purified by chromatography (50 g of silica gel 60 (Merck), chloroform). Colorless oil. Yield: 0.50 g (80%). n_D^{20}: 1.4856. ^{1}H NMR (CDCl$_3$): δ = 2.91 (t; 7 Hz, 2H, thiophene-CH$_2$), 3.37 (s; 3H, OCH$_3$), 3.58 (t; 7 Hz, 2H, CH$_2$O), 6.94 (m; 2H, thiophene), 7.245 (m; 1H, thiophene) [the NMR data are comparable with those in the literature[14]].

2.3. Electrochemical Polymerization: Experimental Conditions. The polymerization was carried out in a conventional, three-electrode electrochemical cell (working, counter, and reference electrodes). The cell was flushed with argon for 5 min to remove oxygen. Electrodes were connected with a potentiostat, a plotter, and a function generator.

General Multisweep Cyclic Voltammetric Conditions. With the help of the function generator, the voltage was linearly increased from the starting potential to a maximum and back to the starting potential. This cycle was repeated several times.

The working electrode was a 19.6 mm^2 platinum plate, the counter electrode a 140 mm^2 platinum plate. The reference electrode had a potential $E_{Ag/AgCl(LiCl/EtOH,s.)}$ = 143 mV against the standard hydrogen electrode. The electrolyte consisted of 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile. The concentration of monomers was 0.05 M, and the scanning rate was 50 mV/s. Before the polymerization was started, the base line was recorded by measuring a cyclic voltammogram in a solution of 0.1 M tetrabutylammonium perchlorate in acetonitrile ($0 < E < 2.5$ V), showing a straight line.

To obtain a smooth, clean electrode surface, the platinum plate was polished with diamond paste (1 μm, Fa.Stuers, Denmark). After polishing, the electrodes were rinsed with distilled water and ethanol and dried in vacuo over silica gel.

Preparation of Larger Films for Chemical Modification. Parallel to the cyclic voltammetry, larger films were prepared for additional characterization and for chemical modification. This electrochemical preparation was carried out on platinum plates with an area of 5.04 cm^2 as anode and cathode. A comparable preparative cell with an analogous three-electrode configuration was applied. Working and counter electrodes were of the same size. Pretreatment of the electrodes was described in the foregoing section.

Electropolymerization of 2, 3, 4, and 5 by Multisweep Cyclic Voltammetry. After the base line was recorded, 7 mL of the 0.05 M monomer solution was placed in a cell and flushed with argon for 5 min. The electrochemical polymerization cycles started at 0 V, rising to the respective maximum of 2.3 V for **2**, 2.4 V for **3**, and 2.2 V for **4**. After one or only a few cycles, the current approached the base line; no reduction was observed.

Formation of a conducting polymer is observed only in the case of 3-(2-methoxyethyl)thiophene (**5**).

Oxidation of the monomer started above a potential of 1.0 V; reduction of the polymer could be observed in a broad cathodic maximum between 1400 and 700 mV when the voltage was decreased. In the following cycles oxidation of the polymer was observed in an anodic current maximum at 900 mV prior to the monomer oxidation with increasing intensity (see Figure 2). Reflection IR: 2926, 2873 ($\nu_{C-H\ aliph}$), 2826 ($\nu_{CH_2OCH_3}$), 1117 cm^{-1} ($\nu_{CH_2OCH_3}$). A cyclic voltammogram of the polymer **6** without monomer is shown in Figure 3.

CH Analysis of the Polymer 6. Anal. Calcd for C_7H_8OS (140.2): C, 59.97; H, 5.75. Found: C, 59.50; H, 5.00.

Measurement of the Thickness of the Polymer Films 6. The thickness of the polymer films were measured by a Minitest 1001 (Elektro-Physik Köln). Respectively, two platinum plates coated with polymer **6** (10 and 15 polymerization cycles) were measured. The thicknesses amounted to (a) 1.2 μm (10 cycles) and (b) 1.7 μm (15 cycles).

Calculation of an Approximate Thickness of the Polymer Films 6. The calculation of an approximate thickness of the separated polymer **6** results from the charge quantity determined from the anodic part of the cyclic voltammogram of **6** after 10 polymerization cycles (84 mC/cm^2). Calculation starts from the suppositions that the reduction of the polymer is based on a two-electron reaction and that approximately 30% of the deposited polymer is electroactive. A rough approximation of the surface coverage of one layer of monomers is 5×10^{-10} mol/cm^2 (assuming a ratio of 1 thiophene molecule per 5 metal atoms), equivalent to 1×10^{-4} C/monolayer. Therefore, after 10 polymerization cycles, a polymer film of **6** consists of approximately 800 monolayers. On the supposition that one monomolecular polymer layer has a thickness of about 10 Å, the rough approximation of the thickness of the polymer film after 10 polymerization cycles is approximately 0.8 μm.

The following investigations were carried out on thin polymer films (two polymerization cycles) which have a thickness of about 200 nm.

Scanning Electron Microscopy (SEM). Scanning electron microscopic (SEM) photographs of the polymers **6**, **7**, and **8** and the immobilized alcohol dehydrogenase were taken with a Hitachi Type S 4000 SEM.

2.4. Reactions of the Polymer Films. Poly[3-(2-hydroxyethyl)thiophene] (7). (A) Ether Cleavage with Hydriodic Acid. A platinum plate coated with poly[3-(2-methoxyethyl)thiophene] (**6**) (two cycles) was treated with 7.6 M fresh distilled hydriodic acid at 126 °C for 5 h. The plate was then removed from the acid, rinsed with distilled water and ethanol, and dried for 1 day in vacuo over silica gel. Reflection IR: 3337 (ν_{OH}), 2960, 2929 cm^{-1} ($\nu_{\mathrm{C-H\ aliph}}$).

(B) Ether Cleavage with Boron Tribromide. A platinum plate coated with poly[3-(2-methoxyethyl)thiophene] (**6**) (two cycles) was treated with 0.95 mL (2.50 g (10 mmol)) of boron tribromide in 5 mL of absolute methylene chloride at room temperature for 5 h. The plate was then removed, hydrolyzed with distilled water, rinsed with ethanol, and dried for 1 day in vacuo over silica gel. Reflection IR: 3336 (ν_{OH}), 2954, 2932 cm^{-1} ($\nu_{\mathrm{C-H\ aliph}}$). A cyclic voltammogram of polymer **7** was recorded (see Figure 4).

Cyclic voltammograms of the polymers after chemical reactions and enzyme immobilization were recorded from a starting potential of 0 V to a potential maximum of 1.4 V.

Poly[3-(2-acetoxyethyl)thiophene] (8). A platinum plate coated with polymer **7** was stirred in a mixture of 10 mL of absolute pyridine and 10 mL of acetic anhydride at room temperature for 20 h. After reaction, the plate was washed with 1 M hydrochloric acid, risned with distilled water, and dried for 1 day in vacuo over silica gel. Reflection IR: 3056 (ν_{arom}), 2958, 2923 ($\nu_{\mathrm{C-H\ aliph}}$) 1738 ($\nu_{\mathrm{C=O}}$), 1240 cm^{-1} ($\nu_{\mathrm{C-O\ ester}}$). A cyclic voltammogram of polymer **8** was recorded between 0.0 and 1.4 V (see Figure 6).

Poly[3-(2-((chlorocarbonyl)oxy)ethyl)thiophene] (9). A platinum plate coated with polymer **7** was stirred in a solution of 0.50 g of triphosgene in 30 mL of dry ether for 3 days at room temperature in a closed flask.

Further reactions should be carried out immediately.

Poly[3-(2-((methoxycarbonyl)oxy)ethyl)thiophene] (10). A platinum plate coated with polymer **9** was stirred in 20 mL of dry methanol for 10 h at room temperature to form polymer **10**. The plate was rinsed 10 times with water, acetone, and ether and dried for 1 day in vacuo over silica gel. Reflection IR: 2954 ($\nu_{\mathrm{C-H\ aliph}}$), 1767 ($\nu_{\mathrm{C=O}}$), 1242 cm^{-1} ($\nu_{\mathrm{C-O\ ester}}$).

Poly[3-(2-((*m*-nitrophenyl)carbamato)ethyl)thiophene] (11). A platinum plate coated with polymer **9** was stirred in a solution of 0.25 g of nitroaniline in 20 mL of dry ether at room temperature for 5 h. After reaction, the plate was washed 5 times with ether, 10 times with distilled water and acetone, and finally dried for 24 h in vacuo over silica gel. Reflection IR: 2957 ($\nu_{\mathrm{C-H\ aliph}}$), 1654 ($\nu_{\mathrm{C=O\ amide}}$), 1531 ($\nu_{\mathrm{NO_2\ asym}}$) 1135 cm^{-1} ($\nu_{\mathrm{NO_2\ sym}}$).

Poly[3-(2-cyanatoethyl)thiophene] (12). In a reaction apparatus with a pH electrode, a plate holder, and a buret, a platinum plate coated with polymer **7** was stirred with a mixture of 300 mg of cyanogen bromide and 7 mL of water. A solution of 2 M sodium hydroxide was added slowly to keep the pH value of the mixture constant at 11.5. After 10 min, the reaction was complete, and the platinum plate was removed and rinsed with distilled water.

Immobilization of Alcohol Dehydrogenase. A platinum plate coated with polymer **12** was agitated with 20 mg of alcohol dehydrogenase (buffer pH 6) at 4 °C for 2 days. After reaction, the plate was removed from the reaction mixture and rinsed with 1 M sodium chloride solution and distilled water. Before the reflection IR spectra was recorded, the sample was dried for 1 day in vacuo over silica gel. IR: 1657 ($\nu_{\mathrm{amide\ I}}$), 1545 cm^{-1} ($\nu_{\mathrm{amide\ II}}$). See Figure 8 for the reflection IR spectrum. A cyclic voltammogram of the immobilized alcohol dehydrogenase was recorded between 0.0 and 1.4 V (see Figure 9).

3. Results and Discussion

3.1. Synthesis of Monomers. Esterification of thiophene-3-acetic acid with methanol in the presence of *p*-toluenesulfonic acid produces methyl thiophene-3-acetate (**1**),[15] which is a suitable starting material for reduction by lithium aluminum hydride[16] or by diisobutylaluminum hydride[17] to form 3-(3-hydroxyethyl)thiophene (**2**) in good yield. **2** is also available from thienyllithium and oxirane.[18] The free hydroxy group of **2** must be protected before starting electrochemical polymerization.

One possibility for protecting was found in the synthesis of the tetrahydropyranyl ether (THP ether) **3**, which succeeds in converting **2** with dihydropyran.[19] The reaction of **2** with hexamethyldisilazane produces the silyl ether **4**,[20] which was also employed as a starting material for polymerization.

3-(2-Methoxyethyl)thiophene (5) is another potential monomer suitable for the production of functionalized polymers.[14] It is synthesized from **2** by methylation with diazomethane.[21]

3.2. Electrochemical Polymerization of 2, 3, 4, and 5. Compounds **2**, **3**, and **4** are investigated under multisweep cyclic voltammetric conditions ($\Delta E = 0{-}2.4$ V). The first cycle depicted an oxidation peak with a maximum at 1.74 V in the case of the hydroxy compound **2**, at 1.78 V in the case of the THP ether **3**, and at 1.75 V in the case of the silyl ether **4**. The peaks shift to lower voltages in the successive cycles; their height decreases and the cyclic voltammogram approximates the base line with the cycles thereafter. No reduction peaks nor visible polymer material was observed at the anode. This behavior is in contrast to the literature[22] for **2**. The colors of the solutions do not change. This experiment was repeated after polishing the anode to remove the thin nonconducting film.

These results may be interpreted as follows: the (tetrahydropyranyl)oxy- and trimethylsilyl groups are reactive in such a way as to interfere with the presumed reaction mechanism of the electrochemical polymerization.[23] There is also the possibility that protons produced during the electrochemical polymerization can cleave the protecting groups of **3** and **4**. Thin films without redox properties can likely be formed at the anode.

Formation of an electrically conducting polymer **6** was observed for the methyl ether **5**, in agreement with the literature[14] (see Figure 1 and Scheme 2).

5 was investigated under multisweep cyclic voltammetric conditions ($\Delta E = 0{-}1.9$ V). The first cycle showed an oxidation peak beginning at 1.0 V, which can be explained as oxidation of the monomer **5**. In the backscan a very broad reduction peak between 1.4 and 0.6 V appeared. A reducible, colored polymer film was obtained at the anode with a first broad maximum around 0.9 V. In the case of reduction, violet streaks appeared in the solution. The electrochemical characterization of this polymer film gave data similar to that described by Lemaire.[14]

A cyclic voltammogram of the polymer film in acetonitrile containing 0.1 M TBAP shows the electrochemical behavior of polymer **6** (see Figure 2). For polymer **6**, the peak potential for oxidation ("doping") (E_{pod}) is observed at 1.09 V and the peak potential for reduction ("dedoping") (E_{prd}) at 1.02 V. The elemental analysis of the separated sample of polymer **6** shows good relations with the presumed composition of the polymer **6** (see Experimental Section).

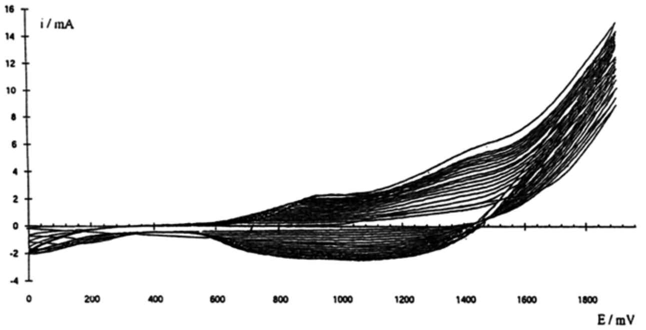
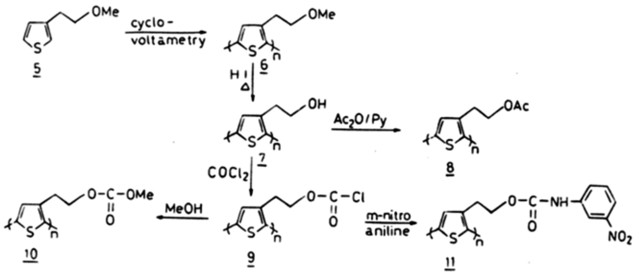


Figure 1. Electrochemical polymerization of 3-(2-methoxyethyl)thiophene (**5**) (1st to 18th cycles).

Scheme 2



The thickness of the polymer film **6** was determined by two different methods: It was measured at the platinum electrode by a Minitest 1001 (Elektro-Physik Köln) and independently calcualted from the cyclic voltammogram.

For the measurements at the platinum electrode it was necessary to produce a thicker film (10 or 15 polymerization cycles). Also the coloumetric analysis of the cyclic voltammogram was carried out for such polymer films (10 polymerization cycles). The two methods, which are in agreement, give a thickness of the polymer film **6** at the electrode of about 0.8–1 μm for 10 polymerization cycles.

Measurements of the FTIR spectra, reactions on the polymer film, and the cyclic voltammograms were carried out on thin polymer layers of **6** (prepared by two polymerization cycles) **7**, and **8** and the layer with the immobilized alcohol dehydrogenase, which have a thickness of about 200 nm (extrapolated from the above-mentioned values).

SEM photographs (see Figure 3) of polymer films **6** may be interpreted as smooth layers covered with additional voluminous depositions.

3.3. Reactions on the Polymer Film 6. Platinum plates were coated with thin polymer films. These films were used for measuring reflection IR spectra studying follow-up reactions. The electrochemical polymerization reaction was completed after two cycles.

A shiny bluish film of polymer **6** was obtained when the polymerization reaction was stopped at 1.9 V (Ag/AgCl) (oxidized form of polymer **6**), and the reddish-golden form of polymer **6** became visible when the cyclic voltammetry was completed at 0 V (reduced form of polymer **6**). The structure of polymer **6** was identified by reflection IR spectroscopy producing a strong signal at 1117 cm^{-1} ($\nu_{\mathrm{C-O-C}}$).

To obtain reactive groups at the surface of the polymer, the ether groups must be converted into hydroxy groups. Two practicable methods of ether cleavage were carried out: with the aid of hydriodic acid[24] and with boron tribromide.[25,26]

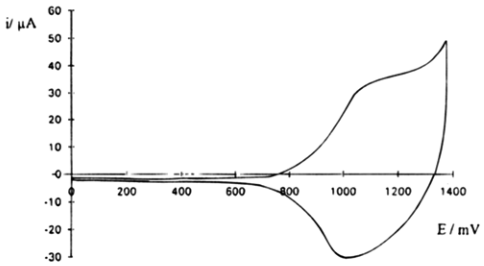


Figure 2. Cyclic voltammogram of poly[3-(2-methoxyethyl)thiophene] (**6**) in 0.1 M TBAP in acetonitrile.

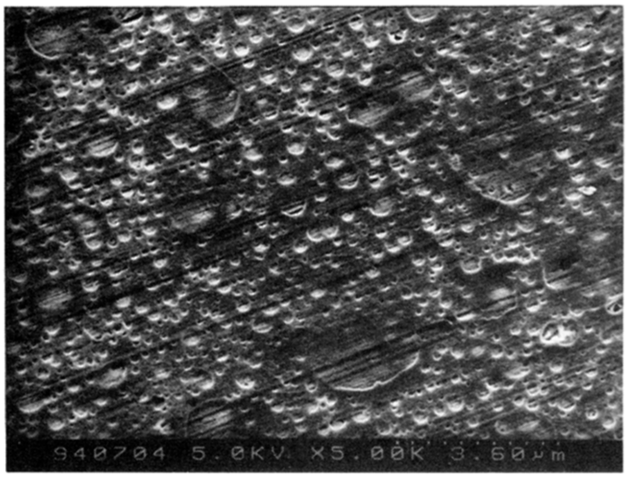


Figure 3. Typical SEM photograph of polymer **6** prepared on platinum plates by cyclic voltammetry (two cycles).

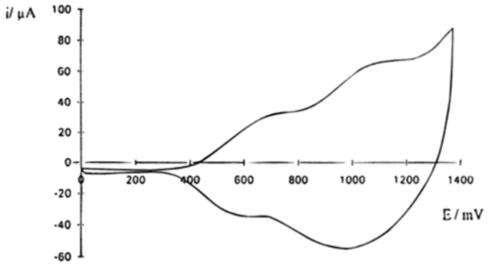


Figure 4. Cyclic voltammogram of poly[3-(2-hydroxyethyl)thiophene] (**7**) in 0.1 M TBAP in acetonitrile.

Due to the drastic conditions of ether cleavage with hydriodic acid, it was expected that the polymer would be destroyed during the reaction. Unexpectedly, however, ether cleavage succeeded through treatment of polymer **6** with hydriodic acid for 5 h at 126 °C, forming poly[3-(2-hydroxyethyl)thiophene] (**7**).

If ether cleavage is carried out with boron tribromide in methylene chloride, similar results are obtained. The polymer layer must be left to mature for some days before treatment because fresh deposited polymer material can be detached from the electrode. Both of these ether cleavage methods give comparable results. In the IR reflectance spectra a broad absorption for hydroxy groups at 3479 cm^{-1} is visible and the strong ether signal at 1117 cm^{-1} disappears completely, indicating a practically quantitative ether cleavage. The cyclic voltammogram of polymer **7** (Figure 4) in acetonitrile containing 0.1 M TBAP shows the electroactivity of the polymer layer (E_{pod} = 1.07 V, E_{prd} = 1.10 V). A new redox peak pair obtained could be connected to the free hydroxy group. This confirms the electroactivity of the polymer after ether cleavage. During some sweeps of the cyclic voltammetric investigation, polymer **7** was

Figure 5. SEM of polymer **7** after ether cleavage of polymer **6**.

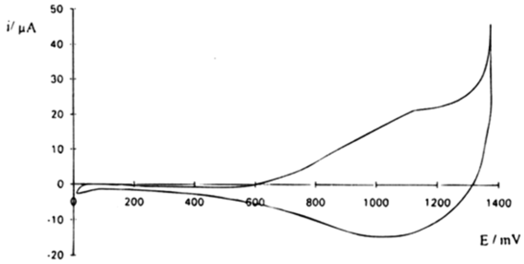


Figure 6. Cyclic voltammogram of poly[3-(2-acetoxyethyl)-thiophene] (**8**) in 0.1 M TBAP in acetonitrile.

Figure 7. SEM of polymer **8** prepared by acetylation of polymer **7**.

irreversibly oxidized, no longer undergoing reactions to the hydroxy groups such as acetylation.

Figure 5 shows the morphology of polymer **7** after ether cleavage. In contrast to Figure 3 the polymer exists as a smooth layer with only some particles.

As an additional indication for the presence of reactive hydroxy groups on the polymer surface and as an example for a derivatization reaction, polymer **7** was treated with acetic anhydride in pyridine,[27] producing polymer **8**, which is also identified by IR reflectance spectroscopy. A strong carbonyl band at 1735 cm^{-1} is typical for the acetate group, whereas the absorption of the hydroxy group at 3479 cm^{-1} is absent.

Figure 6 shows the electrochemcial behavior of the acetoxy polymer **8** (E_{pod} = 1.12 V, E_{prd} = 0.99 V). The oxidation/reduction peaks are less pronounced and the morphology of the polymer is very irregular as shown in Figure 7. In comparison with Figure 5, no characteristic change was observed.

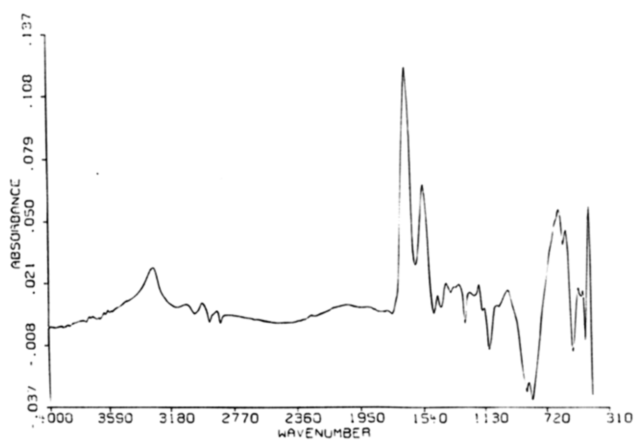


Figure 8. Reflection IR spectrum of immobilized alcohol dehydrogenase.

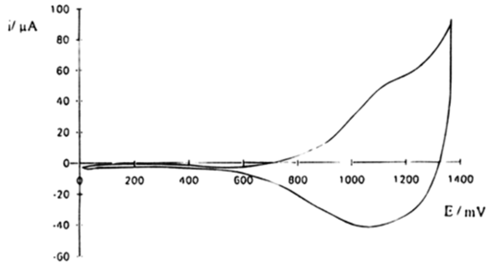
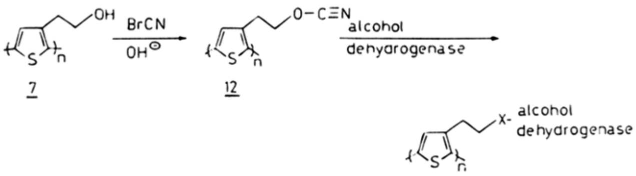


Figure 9. Cyclic voltammogram of immobilized alcohol dehydrogenase in 0.1 M TBAP in acetonitrile.

Scheme 3



The formation of the ester chloride **9**[28] can be considered as an analogous reaction to the Merrifield reactions in protein chemistry for immobilization experiments of amino acids, proteins, and other biologically interesting materials. Conversion of hydroxy polymer **7** with triphosgene in dry ether[29] produces polymer **9**, which is sensitive to hydrolysis and can be reacted with alcohols such as methanol to give polymer **10** or with amines such as *m*-nitroaniline to form polymer **11** as an example for polymers with potential nonlinear optical properties. Details of the structure of these polymers are found by FTIR spectroscopy (carbonyl absorption at 1767 cm^{-1} for polymer **10** and carbon–amide absorption at 1654 cm^{-1} for polymer **11**).

Activation of the hydroxy groups of polymers with cyanogen bromide is a classical method already applied for the immobilization of enzymes.[30,31] Hydroxy polymer **7** reacts in the first step with cyanogen bromide at pH 11.5 in aqueous solution to produce the isocyanate polymer **12**, which can form covalent bonds with hydroxy, mercapto, and amino groups of enzymes[31] (Scheme 3).

By applying this method to conducting polymer films, alcohol dehydrogenase was successfully immobilized to

Figure 10. SEM of polymer **7** after the immobilizing step of alcohol dehydrogenase.

polymer **12**. In the FTIR spectrum two strong bands are visible at 1657 and 1545 cm^{-1} (amide I and II) (Figure 8). This enzyme-coated electrode is under investigation as a redox sensor system.

A cyclic voltammogram of the polymer film in acetonitrile after the immobilizing step with alcohol dehydrogenase shows the electrochemical behavior activity of the electrode (Figure 9) ($E_{\text{pod}} = 1.17$ V, $E_{\text{prd}} = 1.07$ V). The cyclic voltammogram is very similar to the CV in Figure 2 except for slightly smaller current density values.

The morphology of the polymer electrode after enzyme immobilization is presented in Figure 10. The photograph shows a characteristic structure similar to that in polymer **7** (see Figure 5) and typical round reliefs of the uppermost polymer layer.

4. Conclusions and Outlook

Starting from poly[3-(2-methoxyethyl)thiophenediyl] (**6**), ether cleavage was carried out. The resulting poly[3-(2-hydroxyethyl)thiophenediyl] (**7**) contains reactive hydroxy groups on its surface.

The reactivity of the free hydroxy groups was proved by model reactions such as the acylation with acetic anhydride. Alcohol dehydrogenase was covalently bound on the surface of the polythiophene electrode by the cyanogen bromide method.

The structures of the differing polymers were characterized by FTIR spectroscopy, and the modified polymer layers were analyzed by cyclic voltammetry to show their electroactivity.

The covalent immobilization of an enzyme on the surface of a polythiophene layer should be an interesting way to produce enzyme electrodes.

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