Reactive Groups on Polymer-Covered Electrodes. 5. Synthesis and Cyclovoltammetric Analysis of 3-Substituted Thiophene Derivatives†

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ABSTRACT: Various functionalized polythiophene films on electrode surfaces were produced by electropolymerization. Starting from 3-(2-hydroxyethyl)thiophene (**1**) different ether and ester derivatives were synthesized: 3-(2-(benzyloxy)ethyl)thiophene (**2**), 3-[2-((triphenylmethyl)oxy)ethyl]thiophene (**3**), 3-[2-((trimethylsilyl)oxy)ethyl]thiophene (**4**), 3-[2-((dimethyl-*tert*-butylsilyl)oxy)ethyl]thiophene (**5**), 3-(2-acetoxyethyl)thiophene (**6**), 3-(2-(benzoyloxy)ethyl)thiophene (**7**), 3-[2-((*p*-nitrobenzoyl)oxy)ethyl]thiophene (**8**), and 3-[2-((3,5-dinitrobenzoyl)oxy)ethyl]thiophene (**9**). Cyclovoltammetric analyses in acetonitrile with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte gave the characteristic peak potentials (E_p's) of the electrochemical oxidation of these monomers. Under our standard conditions homopolymerization of the monomers **2**−**9** could not be achieved, whereas copolymerization of **2**−**9** with 3-methylthiophene (**10**) was successful. The resulting polymeric films were characterized by FT IR spectroscopy and chemical reactions.

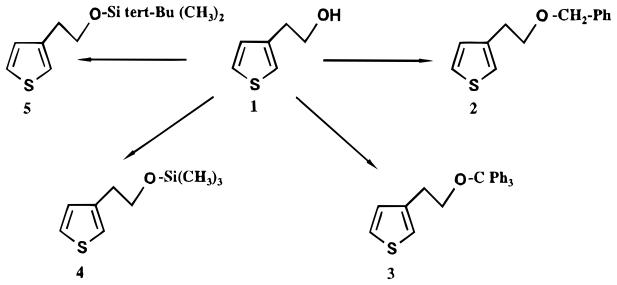
1. Introduction

A new and interesting method for immobilizing biomolecules is covalent binding to electrochemically conducting polymers with reactive groups. In the beginning of the 1980s it was shown that heterocyclics like thiophene and furan derivatives can be polymerized electrochemically.[1] The advantage of electrochemical polymerization lies in the ability to form adhering films with a high solid-state order and good conductivity.[2,3] Several publications describe the electrochemical polymerization of various thiophene derivatives.[4] Most of the derivatives contain no chemically reactive groups because such substituents are known to interfere with the polymerization reaction, resulting in thin nonconducting films on the electrode surface.

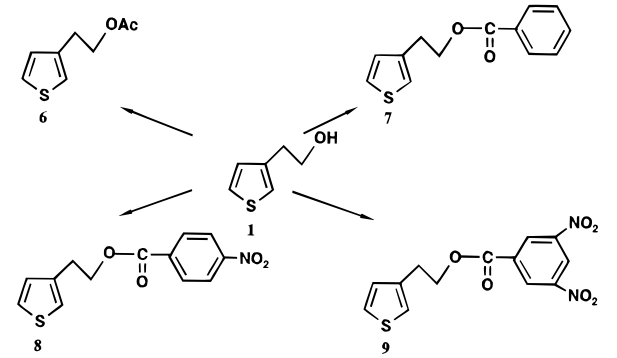
It is possible to synthesize polymers and copolymers of thiophene with reactive carboxylic groups.[5−7] Aminofunctionalized polypyrrole films with different thicknesses have also been used for the covalent binding of glucose oxidase to electrode surfaces.[8,9] New enzyme electrodes can be obtained by electrochemical copolymerization of bipyridine derivatives of pyrrole, *N*-methylpyrrole, and pyrrole-modified glucose oxidase, leading to tertiary copolymers simultaneously integrating redox relays and enzyme activity.[10] Polythiophene derivatives with reactive hydroxy groups can be produced by ether cleavage of polythiophene derivatives containing methyl ether groups under drastic chemical conditions.[11] Alcohol dehydrogenase was successfully immobilized on the surface of such reactive polythiophene films.[11]

A promising way to produce polythiophene derivatives with hydroxy groups under mild chemical conditions is to use 3-(2-hydroxyethyl)thiophene (**1**) as the starting material because it can be protected in several ways. From **1**, the four ethers **2**−**5** with differing hydrolytical stabilities under acid conditions (Scheme 1) and the four esters **6**−**9** (Scheme 2) were synthesized. Electropolymerization and copolymerization of the protected thiophene derivatives **2**−**9** were studied. Homopolymerization of **2**−**9** under our standard conditions was not successful. During the homopolymerization of ethers **2**−**5** only insulating depositions were observed on the electrode which were not identified as polythiophene derivatives by IR spectroscopy. In the case of the homopolymerization experiments for esters **6**−**9** no polymers and no depositions were observed on the electrodes under our polymerization conditions. Copolymerization of **2**−**9** with 3-methylthiophene (**10**) was studied. The copoly-

Scheme 1



Scheme 2



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meric samples were hydrolyzed (cleavage of the protecting groups) and reacted with acetic anhydride and *p*-nitrobenzoyl chloride. The resulting products were characterized by their FT IR spectra.

2. Experimental Section

2.1. Analytical Methods. The ^{1}H NMR spectra were recorded on a Bruker AM 270 or on a Bruker AC 250. Chemical shifts are expressed in δ relative to tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on a Bruker AC 250.

IR spectra were recorded for films or for KBr pellets using a Perkin Elmer 580 B with data station PE 3600. Reflection IR spectra on metal surfaces were recorded by a NICOLET FT IR spectrometer. MS data of the monomers were obtained on a Finnigan MAT 112 and a Finnigan MAT 711. Elemental analyses were performed on a Perkin Elmer 2400 CHN analyzer. Melting points were measured on a Reichert Thermovar. Refractive indices were measured on a Carl Zeiss refractometer. Thin layer chromatography was carried out with TLC aluminum sheets of silica gel 60 F_{254} (Merck, Darmstadt); thiophene derivatives were identified with an acid solution of isatine, and other substances, by development in an iodine atmosphere. Scanning electron microscopy (SEM) photographs were taken with a Hitachi 4000. All photographs were taken at voltages of 5000 V directly from the copolymer electrodes without coating. The electrochemical investigations were carried out with a Heka 510 potentiostat/function generator and a Siemens Kompensograph C 1020.

2.2. Synthesis of the Monomers. 3-(2-Hydroxyethyl)-thiophene (1) was prepared by reduction of 3-thiopheneacetic acid with lithium aluminum hydride.[12] Colorless liquid. Yield: 63%. n^{20}_D: 1.5520. Bp: 110−111 °C/19 mbar. The spectroscopical data are identical to those of ref 11. ^{13}C NMR ($CDCl_3$): δ = 33.4 (1C, C_5), 62.6 (1C, C_6), 121.4 (1C, C_1), 125.6 (1C, C_4), 128.2 (1C, C_3), 138.7 ppm (1C, C_2).

3-(2-(Benzyloxy)ethyl)thiophene (2) was prepared by WILLIAMSON synthesis, as described by Lemaire et al.[13] from **1** and benzyl bromide. Colorless liquid. Yield: 71%. Bp: 140 °C/21 mbar. n^{20}_D: 1.5662. The ^{1}H NMR data are comparable to those of ref 13. ^{13}C NMR ($CDCl_3$): δ = 30.7 (1C, C_5), 70.4 (1C, C_7), 72.9 (1C, C_6), 121.1 (1C, C_1), 125.1 (1C, C_4), 127.5 (2C, C_9), 127.5 (1C, C_{11}), 128.3 (2C, C_{10}), 128.4 (1C, C_3), 138.3 (1C, C_2), 139.1 ppm (1C, C_8). MS (70 eV): 218 (3), M^+; 112 (70), $[(M + 1) - C_6H_5 - OCH_2]^+$; 111 (5), $(M - C_6H_5 - OCH_2)^+$; 98 (8), $[(M + 1) - CH_2 - C_6H_5 - OCH_2]^+$; 97 (100), $(M - CH_2 - C_6H_5 - OCH_2)^+$; 92 (8) $[(M + 1) - O(CH_2)_2 - C_4H_3S]^+$; 91 (95), $[M - O(CH_2)_2 - C_4H_3S]^+$; 77 (4), $[M - O(CH_2)_2 - C_4H_3S]^+$; 65 (8), $[M - CH_2 - O(CH_2)_2 - C_5H_3S]^+$; 51 (3), $[M - CH_2 - C_2H_2 - O(CH_2)_2 - C_4H_3S]^+$; 45 (4), $[M - CH_2 - C_3H_2 - C_6H_5 - O(CH_2)_2]^+$; 39 (4), $[M - CH_2 - C_3H_2 - O(CH_2)_2 - C_4H_3S]^+$. IR (film): 3103−3030 (m, ν(C−H arom)), 2916, 2857 (s, ν(C−H aliph)), 1603, 1586, 1537 (w, ν(C=C arom)), 1453 (s, δ(C−H aliph)), 1102 (s, ν(C−O ether)), 1028 (m, ν(C−S arom)), 775 (s, thiophene), 736, 698 cm^{-1} (s, benzene). Anal. Calcd for $C_{13}H_{14}OS$ (218.1): C, 71.53; H, 6.47. Found: C, 71.05; H, 5.77.

3-[2-((Triphenylmethyl)oxy)ethyl]thiophene (3). Triphenylmethyl chloride was added to a solution of 1 g (7.8 mmol) of **1** in 5 mL of pyridine. The solution was stirred at 90 °C for 24 h and mixed with 10 mL of ice water. The crude yellow ether **3** was dissolved in diethyl ether, separated from the aqueous phases, and washed with 5 mL of cold diluted hydrochloric acid, saturated sodium hydrogen carbonate solution, and water. The ether extract was dried over magnesium sulfate and concentrated in vacuo. The pale yellow raw material [yield: 2.55 g (88%)] was purified by chromatography (100 g of silica gel 60 MERCK, hexane). Colorless crystals. Yield: 1.03 g (36%). Mp: 103−105 °C. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 2.92 (t, J = 6.25 Hz, 2H, CH_2 thiophene), 3.28 (t, J = 6.25 Hz, 2H, CH_2O), 6.96 (dd, $^3J_{bc}$ = 5.6 Hz, $^4J_{ba}$ = 2.5 Hz, 1H, thiophene (b)), 7.0 (dd, $^4J_{ca}$ < 1 Hz, $^4J_{ba}$ = 2.5 Hz, 1H, thiophene (a)), 7.16−7.4 ppm (m, 15H + 1H, phenyl + thiophene (c)). ^{13}C NMR ($CDCl_3$): δ = 31.0 (1C, C_5), 64.2 (1C, C_7), 86.6 (1C, C_6), 121.3 (1C, C_1), 125.0 (1C, C_4), 126.8 (1C, C_{11}), 127.7 (1C, C_3), 128.3 (2C, C_9), 128.6 (2C, C_{10}), 139.6 (1C, C_2), 144.2 ppm (1C, C_8). MS (70 eV): 370 (3), M^+; 259 (5), $(M - C_2H_4 - C_4H_3S)^+$; 244 (24), $(M - C_2H_4 - C_4H_3S)^+$; 243 (100), $[M - O(CH_2)_2 - C_4H_3S]^+$; 166 (4), $[M - C_6H_5 - O(CH_2)_2 - C_4H_3S]^+$; 165 (25), $[M - H - C_6H_5 - O(CH_2)_2 - C_4H_3S]^+$; 111 (19), $[M - OC(C_6H_5)_3]^+$; 105 (7), $[M - 2(C_6H_5) - O(CH_2)_2 - C_4H_3S]^+$; 97 (4), $[M - C(C_6H_5)_3 - OCH_2]^+$; 77 (5), $[M - C(C_6H_5)_2 - O(CH_2)_2 - C_4H_3S]^+$; 45 (1) $[M - C_3H_2 - C(C_6H_5)_2 - O(CH_2)_2]^+$. IR (KBr): 3088−3018 (m, ν(C−H arom)), 2952−2873 (m, ν(C−H aliph)), 1596, 1562, 1536 (w, ν(C=C arom)), 1490, 1448 (s, δ(C−H aliph)), 1066 (s, ν(C−O ether)), 1030 (w, ν(C−S arom)), 788 (s, thiophene), 764, 700 (s, benzene), 720 cm^{-1} (w, δ(C−H rocking aliph)). Anal. Calcd for $C_{25}H_{22}OS$ (370.1): C, 81.05; H, 5.99. Found: C, 81.20; H, 6.11.

3-[2-((Trimethylsilyl)oxy)ethyl]thiophene (4). Two grams (15.6 mmol) of **1** was added to 10 mL of a mixture of pyridine/hexamethyldisilazane/trimethylchlorsilane (9/3/1) and stirred at room temperature for 7 days. The resulting suspension was distilled in vacuo (bp: 114 °C/10 mbar), and the raw material [yield: 2.5 g (80%)] was purified by chromatography [100 g of silica gel 60 MERCK, hexane/ethyl acetate (9/1)]. Colorless liquid. Yield: 1.6 g (51%). Bp: 114 °C/10 mbar. n^{20}_D: 1.5446. The spectroscopical data are identical to those of ref 11. ^{13}C NMR ($CDCl_3$): δ = −0.6 (3C, C_7), 33.7 (1C, C_5), 63.0 (1C, C_6), 121.2 (1C, C_1), 125.1 (1C, C_4), 128.5 (1C, C_3), 139.2 ppm (1C, C_2).

3-[2-((Dimethyl-*tert*-butylsilyl)oxy)ethyl]thiophene (5). Imidazole (3.44 g, 50.6 mmol) was added to a solution of 2.00 g (15.6 mmol) of **1** and 3.43 g (22.9 mmol) of dimethyl-*tert*-butylchlorosilane in 20 mL of dimethylformamide. The solution was stirred for 24 h and afterward washed with 100 mL of saturated sodium hydrogen carbonate solution and four times with respectively 40 mL of hexane. The collected organic extracts were washed with water, dried over magnesium sulfate, and concentrated in vacuo. The raw material [yield: 2.48 g (65%)] was purified by chromatography [120 g of silica gel 60 MERCK, hexane/ethyl acetate (19/1)]. Colorless liquid. Yield: 1.94 g (51%). Bp: 120 °C/9 mbar. n^{20}_D: 1.4853. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.04 (s, 6H, $Si(CH_3)_2$), 0.92 (s, 9H, $SiC(CH_3)_3$), 2.87 (t, J = 6.25 Hz, 2H, CH_2-thiophene), 3.82 (t, J = 6.25 Hz, 2H, CH_2O), 6.96−7.01 (m, 2H, thiophene (a,b)), 7.2−7.26 ppm (m, 1H, thiophene (c)). ^{13}C NMR ($CDCl_3$): δ = −5.4 (2C, C_7), 18.3 (1C, C_8), 25.9 (3C, C_9), 33.8 (1C, C_5), 63.7 (1C, C_6), 121.2 (1C, C_1), 124.9 (1C, C_4), 128.7 (1C, C_3), 139.4 ppm (1C, C_2). MS (70 eV): 242 (0.1), M^+; 227 (3), $(M - CH_3)^+$; 186 (20), $[(M + 1) - C(CH_3)_3]^+$; 185 (100), $[M - C(CH_3)_3]^+$; 167 (23), $[M - (CH_3)_5]^+$; 111 (31), $[M - OSi(CH_3)_2C(CH_3)_3]^+$; 75 (16), $[(M + 1) - C_2H_4 - C(CH_3)_3 - C_4H_3S]^+$; 73 (17), $[M - C(CH_3)_2 - O(CH_2)_2 - C_4H_3S]^+$. IR (film): 3107, 3053 (w, ν(C−H arom)), 2955−2857 (s, ν(C−H aliph)), 1537 (w, ν(C=C arom)), 1472, 1463 (m, δ(C−H aliph)), 1389, 1361 (s, δ(C−H *tert*-butyl)), 1101 (s, ν(C−O ether)), 1044 (w, ν(C−S arom)), 775 (s, thiophene), 732 cm^{-1} (w, δ(C−H rocking aliph)). Anal. Calcd for $C_{12}H_{22}OSSi$ (242.1): C, 59.48; H, 9.16. Found: C, 58.72; H, 8.54.

3-(2-Acetoxyethyl)thiophene (6). Two grams (15.6 mmol) of **1** was dissolved in 5.43 g (53.2 2 mmol) of acetic anhydride and 5 mL of absolute pyridine. After a reaction time of 24 h the solution was added to 50 mL of ice water. The mixture was washed five times with diethyl ether. The collected organic extracts were washed with 40 mL of 10% hydrochloric acid and saturated sodium hydrogen carbonate solution. The ether extracts were dried over magnesium sulfate and concentrated in vacuo. Raw **6** [yield: 2.3 g (86%)] was purified by distillation in vacuo. Colorless liquid. Yield: 1.52 g (57%). Bp: 109 °C/9 mbar. n^{20}_D: 1.5098. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 2.08 (s, 3H, COH_3), 2.98 (t, J = 6.25 Hz, 2H, CH_2-thiophene), 4.32 (t, J = 6.25 Hz, 2H, CH_2O), 6.96 (dd, $^4J_{ba}$ = 2.5 Hz, $^3J_{bc}$ = 5 Hz, 1H, thiophene (b)), 7.04 (dd, $^4J_{ab}$ = 2.5 Hz, $^4J_{ac}$ = 1 Hz, 1H, thiophene (a)), 7.28 ppm (dd, $^4J_{ca}$ = 1 Hz, $^3J_{cb}$ = 5 Hz, 1H, thiophene (c)). ^{13}C NMR ($CDCl_3$): δ = 20.5 (1C, C_8), 29.2 (1C, C_5), 63.9 (1C, C_6), 121.2 (1C, C_1), 125.3 (1C, C_4), 127.9 (1C, C_3), 137.7 (1C, C_2), 170.5 ppm (1C, C_7). MS (70 eV): 170 (1), M^+; 112 (4), $[(M + 1) - CH_3 - COO]^+$; 111 (27), $(M - CH_3 - COO)^+$; 110 (100), $(M - CH_3 - COOH)^+$; 98 (9), $[(M< + 1) - C_2H_5 - COO]^+$; 97 (68), $(M - C_2H_5 - COO)^+$; 45 (13), $(M - C_6H_9 - COO)^+$; 43 (76), $[M - O(CH_2)_2 - C_4H_3S]^+$. IR (film): 3457 (w, ν(O−H)), 3103, 3053 (m, ν(C−H arom)), 2958, 2901 (m, ν(C−H aliph)), 1739 (s, ν(C=O ester)), 1622,

1571, 1537 (w, ν(C═C arom)), 1468−1432, 1383 (m, s, δ(C−H aliph)), 1363 (s, ν(C−H acetate)), 37, 1035 (s, ν(C−O ester)), 1067 (s, ν(C−S arom)), 777 cm^{-1} (s, thiophene). Anal. Calcd for $C_8H_{10}O_2S$ (170.0): C, 56.46; H, 5.93. Found: C, 57.01; H, 6.64.

3-(2-(Benzoyloxy)ethyl)thiophene (7), 3-[2-(*p*-nitrobenzoyl)ethyl]thiophene (8), and 3-[2-((3,5-dinitrobenzoyl)-oxy)ethyl]thiophene (9). The acyl chloride (20 mmol, 2.80 g of benzoyl chloride, 37.0 g of *p*-nitrobenzoyl chloride, or 4.60 g of 3,5-dinitrobenzoyl chloride) was added to a solution of 2.00 g (15.6 mmol) of **1** in 5 mL of absolutely water-free pyridine under cooling and stirring. After 24 h for **7** or 48 h for **8** and **9** the reaction mixture was poured into 50 mL of ice water. The aqueous phase was extracted 5 times with diethyl ether, and the collected organic extracts were washed with 10% hydrochloric acid and saturated sodium hydrogen carbonate solution, dried over magnesium sulfate, and concentrated in vacuo. Raw **7** [yield: 86% (3.80 g)] was purified by chromatography [120 g of silica gel 60 MERCK, hexane/ethyl acetate (9/1)]. Raw **8** [yield: 82% (4.15 g)] and **9** [yield: 82% (4.15 g)] were purified by twofold recrystallization from ethanol.

3-(2-(Benzoyloxy)ethyl)thiophene (7). Colorless syrupy liquid. Yield: 1.17 g (31%). Bp: 185 °C/10 mbar. n^{20}_D = 1.5729. ^{1}H NMR ($CDCl_3$ 270 MHz): δ = 3.12 (t, J = 6.25 Hz, 2H, CH_2-thiophene), 4.52 (t, J = 6.25 Hz, 2H, CH_2O), 7.03 (m, 1H, thiophene (b)), 7.08 (m, 1H, thiophene (a)), 7.24−7.31 (m, 1H, thiophene (c)), 7.38−7.46 (m, 2H, phenyl (b)), 7.52−7.58 (m, 1H, phenyl (a)), 8.0−8.04 ppm (m, 2H, phenyl (c)). ^{13}C NMR ($CDCl_3$): δ = 29.6 (1C, C_5), 67.8 (1C, C_6), 121.6 (1C, C_1), 125.6 (1C, C_4), 128.2 (1C, C_3), 128.3 (2C, C_{10}), 129.5 (2C, C9), 130.2 (1C, C_8), 132.9 (1C, C_{11}), 138.0 (1C, C_2), 166.4 ppm (1C, C_7). MS (70 eV): 232 (0.2), $(M)^+$; 112 (6), $[(M + 1) - C_6H_5 - COO]^+$; 111 (11), $(M - C_6H_5 - COO]^+$; 110 (100), $(M - C_6H_5 - COOH)^+$; 105 (46), $[M - O(CH_2)_2 - C_4H_3S]^+$; 97 (6), $(M - CH_2 - C_6H_5 - COO)^+$; 78 (3), $[(M + 1) - C_2H_4 - COO - C_4H_3S]^+$; 77 (29), $(M - C_2H_4 - COO - C_4H_3S)^+$; 51 (4), $(M - C_4H_6 - COO - C_4H_3S)^+$; 45 (3), $(M - C_5H_6 - C_6H_5 - COO)^+$. IR (film): 3105, 3062 (w, ν(C−H arom)), 2957−2897 (w, ν(C−H aliph)), 1718 (s, ν(C═O ester)), 1602, 1584, 1537 (w, ν(C═C arom)), 1467−1451 (s, δ(C−H aliph)), 1273, 1115 (s, ν(C−O ester)), 1070 (m, ν(C−S arom)), 777 (s, thiophene), 712, 687 cm^{-1} (s, benzene). Anal. Calcd for $C_{13}H_{12}O_2S$ (232.1): C, 67.23; H, 5.21. Found: C, 67.02; H, 4.21.

3-[2-((*p*-Nitrobenzoyl)oxy)ethyl]thiophene (8). Orange crystals. Yield: 1.63 g (37%). Mp: 79 °C. ^{1}H NMR ($CDCl_3$ 270 MHz): δ = 3.14 (t, J = 7.5 Hz, 2H, CH_2-thiophene), 4.58 (t, J = 7.5 Hz, 2H, CH_2O), 6.98−7.08 (m, 2H, thiophene (a,b)), 7.24−7.28 (m, 1H, thiophene (c)), 8.16 (d, J = 7.5 Hz, 2H, phenyl (b,b′)), 8.26 ppm (d, J = 7.5 Hz, 2H, phenyl (a,a′)). ^{13}C NMR ($CDCl_3$): δ = 29.5 (1C, C_5), 64.8 (1C, C_6), 121.7 (1C, C_1), 123.5 (2C, C_{10}), 125.9 (1C, C_4), 128.1 (1C, C_3), 130.6 (2C, C_9), 135.5 (1C, C_8), 137.5 (1C, C_2), 150.5 (1C, C_{11}), 164.5 ppm (1C, C_7). MS (70 eV): 277 (0.2), M^+; 150 (12), $[M - O(CH_2)_2 - C_4H_3S]^+$; 112 (5), $[(M + 1) - CH_2 - C_6H_5 - COO - NO_2]^+$; 111 (9), $(M - CH_2 - C_6H_5 - COO - NO_2)^+$l; 110 (100), $(M - C_6H_5 - COOH - NO_2]^+$; 104 (10), $[M - O(CH_2)_2 - C_4H_3S - NO_2]^+$; 97 (14), $(M - CH_2 - C_6H_5 - COO - NO_2)^+$; 76 (5), $[M - (CH_2)_2 - COO - C_4H_3S - NO_2]^+$; 45 (2), $(M - C_5H_6 - C_6H_5 - COO - NO_2)^+$. IR (KBr): 3419 (w, ν(O−H)), 3106−3054 (w, ν(C−H arom)), 3000−2862 (w, ν(C−H aliph)), 1717 (s, ν(C═O ester)), 1608, 1573 (m, ν(C═C arom)), 1528, 1350 (s, ν(N−O)), 1456 (m, δ(C−H aliph)), 1268, 1100 (s, ν(C−O ester)), 1047 (m, ν(C−S arom)), 838 (benzene), 785 cm^{-1} (m, thiophene). Anal. Calcd for $C_{13}H_{11}NO_4S$ (277.0): C, 56.31; H, 4.00. Found: C, 56.01; H, 4.03.

3-[2-((3,5-Dinitrobenzoyl)oxy)ethyl]thiophene (9). Orange crystals. Yield: 1.9 g (37%). Mp: 108 °C. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 3.18 (t, J = 7.25 Hz, 2H, CH_2-thiophene), 4.6 (t, J = 7.25 Hz, 2H, CH_2O), 6.96−7.08 (m, 2H, thiophene (a,b)), 7.24−7.3 (m, 1H, thiophene (c)), 9.1 (d, J = 2.5 Hz, 2H, phenyl (b,b′)), 9.2 ppm (t, J = 2.5 Hz, 1H, phenyl (a)). ^{13}C NMR ($CDCl_3$): δ = 29.4 (1C, C_5), 66.5 (1C, C_6), 121.9 (1C, C_1), 122.3 (1C, C_{11}), 126.1 (1C, C_4), 128.0 (1C, C_3), 129.3 (2C, C_9), 133.8 (1C, C_8), 137.0 (1C, C_2), 148.6 (2C, C_{10}), 162.3 ppm (1C, C_7). MS (70 eV): 322 (1), $(M)^+$; 195 (6), $[M - O(CH_2)_2 - C_4H_3S]^+$; 149 (6), $[M - O(CH_2)_2 - C_4H_3S - NO_2]^+$; 112 (5), $[(M + 1) - C_6H_3 - COO - (NO_2)_2]^+$; 111 (9), $[M - C_6H_3 - COO - (NO_2)_2]^+$; 10 (100), $[M - C_6H_3 - CIOOH - (NO_2)_2]^+$; 97 (31), $[M - C_6H_3 - COO - (NO_2)_2]^+$; 75 (8), $[M - C_2H_4 - COO - C_4H_3S - (NO_2)_2]^+$; 45 (3), $[M - C_2H_4 - C_6H_3 - COO - C_3H_2S - (NO_2)_2]^+$. IR (KBr): 3108, 3084 (m, ν(C−H arom)), 2962−2876 (w, ν(C−H aliph)), 1730 (s, ν(C═O ester)), 1628, 1595 (m, ν(C═C arom)), 1546, 1343 (s, ν(N−O)), 1460−1444 (m, δ(C−H aliph)), 1277, 1163 (s, ν(C−O ester)), 1075 (m, ν(C−S arom)), 892 (w, 1,3,5-substituted benzene), 775 cm^{-1} (m, thiophene). Anal. Calcd for $C_{13}H_{10}N_2O_6S$ (322.0): C, 48.44; H, 3.13. Found: C, 48.37; H, 3.11.

Table 1. Oxidation Potentials of the Monomers (2−9)

substance	oxidation potential (E_{pox})
2	1.86
3	1.98
4	1.75
5	1.88
6	2.49
7	2.31
8	2.35
9	2.29

2.3. Cyclic Voltammetric Conditions. The cyclic voltammetric measurements were carried out in conventional, three-electrode cells (working, counter, and reference electrode). The cells were flushed with argon for 5 min before measuring to remove oxygen. With the help of a function generator, the voltage was linearly changed from the starting potential to a maximum and back to the starting potential. This cycle was repeated several times. Working and counter electrodes are of platinum, as described below. The Ag/AgCl reference electrode E(Ag/AgCl (LiCl/EtOH,s)) = 143 mV against the standard hydrogen electrode. The electrolyte consists of 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile; the scanning rate was 50 mV/s. Before the electrochemical investigation of the monomers or the copolymerization experiments were started, the base line was recorded by measuring a cyclic voltammogram of a solution of TBAP in acetonitrile ($-0.143 < E < 2.6$ V), showing a straight line. In order to obtain a smooth, clean electrode surface the platinum electrodes were polished with diamond paste (1 μm Stuers, Denmark). Additionally the electrodes were treated with sulfuric and nitric acids for 5 h followed by rinsing with distilled water and ethanol. Electrodes were dried over silica gel in vacuo before starting the electrochemical investigation or the copolymerization experiments.

2.4. Electrochemical Investigation of the Monomers and Copolymerization Experiments. The monomers were investigated under cyclic voltammetric conditions as described in section 2.3 at concentrations of 0.05 M. The working electrode was a 19.6 mm^2 platinum plate, and the counter electrode, a platinum wire with a diameter of 0.5 mm and a length of 20 mm. The peak potentials for oxidation are shown in Table 1, determined at a potential range of $\Delta E = -0.143$ to 2.2 V for the ethers and −0.143 to 2.6 V for the esters. Homopolymerization was studied at stepwise decreasing oxidation potentials down to the respective peak potentials of the compounds.

Copolymerization experiments were carried out with 3-methylthiophene (**10**) and the corresponding ethers **2**−**5** and esters **6**−**9** both in concentrations of 0.05 M under cyclic voltammetric conditions. The equipment was the same as in the investigations of the monomers. The copolymerization was finished at −0.143 V to produce the reduced form of the copolymer. The different potential ranges are presented below together with the FT IR data. After preparation, the copolymers were washed with acetonitrile and ether to remove monomers and soluble oligomer traces. The cyclic voltammetric investigation of the copolymers in monomer-free solution at a potential range from −0.143 up to 1.4 V gave the oxidation and reduction potentials of the copolymers which are listed in Table 2 (see also Figure 6 with five redox cycles of copolymer **16**).

Larger films for recording the reflection IR spectra and for the chemical modification were prepared on platinum plates with an area of 5.04 cm^2 as anode and cathode in a comparable preparative cell with an analogous three-electrode configuration.

Table 2. Oxidation and Reduction Potentials of the Copolymers (11−19)

copolymer	starting monomers	oxidation potential (E_{pox})	reduction potential (E_{pred})
11	**2** + **10**	1.27	0.97
12	**3** + **10**	1.08	0.90
13	**4** + **10**	1.14	0.96
14	**5** + **10**	0.97	0.80
15	**6** + **10**	0.71	0.45
16	**7** + **10**	1.18	0.62
17	**8** + **10**	1.19	0.54
18	**9** + **10**	0.91	0.49
19[b]			0.90
15[a]		1.22	0.96
17[b]		1.11	0.86

[a] Produced by reaction of copolymer **14**. [b] Produced by reaction of copolymer **15**.

Reflection IR spectra show characteristic bands for the 3-substituted thiophene units which are incorporated in the copolymers:

Copoly[3-(2-(benzyloxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**11**) (ΔE = −0.143 to 2.0 V). Reflection IR: 2937, 2861 (ν(C−H aliph)), 1496, 1454, 1397, 1340 (δ(C−H aliph)), 1103 (ν(C−O ether)), 1030 (ν(C−S arom)), 840 (δ(2,3,5-subst thiophene)), 742, 700 cm^{-1} (δ(subst arom)).

Copoly[3-(2-((triphenylmethyl)oxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**12**) (ΔE = −0.143 to 2.0 V). Reflection IR: 3076 (ν(C−H arom)), 2941, 2869 (ν(C−H aliph)), 1431, 1339 (δ(C−H aliph)), 1119 cm^{-1} (ν(C−O ether)).

Copoly[3-(2-((trimethylsilyl)oxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**13**) (ΔE = −0.143 to 1.8 V). Reflection IR: 2939 (ν(C−H arom)), 1422, 1326 (δ(C−H aliph)), 1100 (ν(C−O ether)), 1041 (ν(C−S arom)), 843 cm^{-1} (δ(2,3,5-subst thiophene)).

Copoly[3-(2-((dimethyl-*tert*-butylsilyl)oxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**14**) (ΔE = −0.143 to 1.9 V). Reflection IR: 3090 (ν(C−H arom)), 2954, 2881 (ν(C−H aliph)), 1443, 1411 (δ(C−H aliph)), 1108 (ν(C−O ether)), 1040 (ν(C−S arom)), 854 cm^{-1} (δ(C−H 2,3,5-subst thiophene)).

Copoly[3-(2-acetoxyethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**15**) (ΔE = −0.143 to 2.0 V). Reflection IR: 3067 (ν(C−H arom)), 2956, 2867 (ν(C−H aliph)), 1743, (ν(C=O ester)), 1445, 1394 (δ(C−H aliph)), 1333 (ν(C−H acetate)), 1245, 1182(ν(C−O ester)), 1040 cm^{-1} (ν(C−S arom)).

Copoly[3-(2-(benzoyloxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**16**) (ΔE = −0.143 to 2.1 V). Reflection IR: 3060 (ν(C−H arom)), 2951, 2925 (ν(C−H aliph)), 1721 (ν(C=O ester)), 1602 (ν(C=C arom)), 1397, 1330 (δ(C−H aliph)), 1275, 1177 (ν(C−O ester)), 1071 (ν(C−S arom)), 839 (δ(C−H 2,3,5-subst thiophene)), 716, 622 cm^{-1} (δ(subst benzene)).

Copoly[3-(2-((*p*-nitrobenzoyl)oxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**17**) (ΔE = −0.143 to 2.1 V). Reflection IR: 2966, 2928 (ν(C−H aliph)), 1727 (ν(C=O ester)), 1609 (ν(C=C arom)), 1529, 1395 (ν(N−O nitro group)), 1395, 1342, 1324 (δ(C−H aliph)), 1274, 1119 (ν(C−O ester)), 1016 (ν(C−S arom)), 838 (δ(C−H 2,3,5-subst thiophene)), 872 cm^{-1} (δ(subst benzene)).

Copoly[3-(2-((3,5-dinitrobenzoyl)oxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**18**) (ΔE = −0.143 to 2.2 V). Reflection IR: 1735 (ν(C=O ester)), 1632 (ν(C=C arom)), 1548, 1346 (ν(N−O nitro groups)), 1459, 1397 (δ(C−H aliph)), 1285, 1170 (ν(C−O ester)), 1101 (ν(C−S arom)), 837 (δ(C−H 2,3,5-subst thiophene)), 867 cm^{-1} (δ(subst benzene)).

Elemental Analyses of Copolymers 17 and 18. Data of **17**: Calcd for $(C_5H_4S)_4(C_{13}H_9NO_4S)(H_2)$ (661.9): C, 59.88; H, 4.11; N, 2.12; S, 23.95. Found: C, 56.22; H, 3.80; N, 1.97; S, 20.45. Data of **18**: Calcd for $(C_5H_4S)_5(C_{13}H_8N_2O_6S)(H_2)$ (803.0): C, 56.84; H, 3.77; N, 3.49; S, 23.95. Found: C, 52.86; H, 3.53; N, 3.60; S, 20.15.

2.5. Reactions of the Polymer Films. Copoly[3-(2-acetoxyethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (15). A platinum plate coated with copoly[3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**14**) was treated with 1 N hydrochloric acid for 1 h. Then the electrode was rinsed off with distilled water, dried in vacuo, and treated with a mixture of 5 mL of acetic anhydride and 5 mL of pyridine at room temperature for 1 h to produce **15**. After reaction the electrode was washed with 1 N hydrochloric acid, ethanol, and ether and dried in vacuo. Reflection IR spectrum of **15** (produced by reaction of copolymer **14**): 3051 (ν(C−H arom)), 2961, 2871 (ν(C−H aliph)), (1734 (ν(C=O acetate)), 1632 (ν(C=C arom)), 1486, 1441 (δ(C−H aliph)), 1371 (ν(C−H acetate)) 1246, 1171 (ν(C−O acetate)), 1027 (ν(C−S arom)), 835 cm^{-1} (δ(2,3,5-subst thiophene)).

Copoly[3-(2-((*p*-nitrobenzoyl)oxy)ethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (17). A platinum plate coated with **15** was treated with 1 N methanolic sodium hydroxide solution containing 10% water for 10 h. The electrode was rinsed off with distilled water and ether and dried in vacuo. The resulting platinum plate coated with copolymer **19** (characterized by its FT IR spectrum) was placed in a solution of 3.7 g of *p*-nitrobenzoyl chloride in 5 mL of pyridine for 8 h. Then the electrode was washed with 1 N hydrochloric acid, distilled water, ethanol, and ether. After drying in vacuo a reflection IR spectrum was taken. Reflection IR spectra: copoly[3-(2-hydroxyethyl)thiophene-2,5-diyl-3-methylthiophene-2,5-diyl] (**19**), 3561 (ν(O−H alcohol)), 2947, 2867 (ν(C−H aliph)), 1351 (δ(C−H aliph)), 1396 (δ(O−H alcohol)), 1151 (ν(C−O alcohol)), 1043 (ν(C−S arom)), 832 cm^{-1} (δ(C−H 2,3,5-subst thiophene)); **17** (produced by reaction of copolymer **15** via **19**), 3111, 3055 (ν(C−H arom)), 1729 (ν(C=O *p*-nitrobenzoate)), 1655, 1608 (ν(C÷xdbdC arom)), 1531, 1348 (ν(N−O nitro group)), 1455, 1413, 1348 (δ(C−H aliph)), 1273, 1117 (ν(C−O ester)), 1016 (ν(C−S arom)), 839 cm^{-1} (δ(2,3,5-subst thiophene)).

3. Results and Discussion

3.1. Synthesis of the Monomers. An usual method to protect alcohols is their conversion into ethers (Scheme 1). Starting from 3-(2-hydroxyethyl)thiophene (**1**) the benzyl ether **2** was synthesized by Williamson ether synthesis.[14] The trityl ether **3** was synthesized by reaction of **1** with trityl chloride.[15] In addition the two silyl ethers **4** and **5** were obtained from **1** by reaction with trimethylsilyl chloride/hexamethyldisilazane/pyridine[16] for **4** and by reaction with *tert*-butyldimethylsilyl chloride/imidazole for **5**.[17] These ethers **2**−**5** are stable in basic medium and have different stabilities against acidic hydrolysis.

The esters **6**−**9** were synthesized by acylation, the acetate **6** was obtained by reaction with acetic anhydride/pyridine,[18] and the esters **7**−**9** were obtained by conversion of **1** with benzoyl chloride and the substituted acid chlorides in pyridine (Scheme 2).[19]

3.2. Electrochemical Investigation and Homopolymerization Experiments. All compounds **2**−**9** were investigated by cyclic voltammetry. To characterize the monomers by their electrochemical behavior, they were oxidized at a potential range starting at −0.143 V up to 2.2 V for the ethers **2**−**5** and up to 2.6 V for the esters **6**−**9**. At these potentials the monomers were overoxidized and no polymerization reactions were observed. Overoxidation gives structures other than the expected and wanted ones. We assume that the aromatic structure of the thiophene units could have been destroyed to become nonconductive. The peak potentials for the oxidation of the monomers are listed in Table 1. The peak potentials of the ethers **2**−**5** are lower than 2.00 V. The highest oxidation potential of the ethers shows the trityl ether **3** at 1.98 V. The oxidation potential of the esters **6**−**9** amounts to more than 2.00 V, influenced by the −*I* effect of the carbonyl group of the substituent. The highest oxidation potential was observed in the case of the acetate **6**, and the oxidation potentials of the esters with phenyl groups

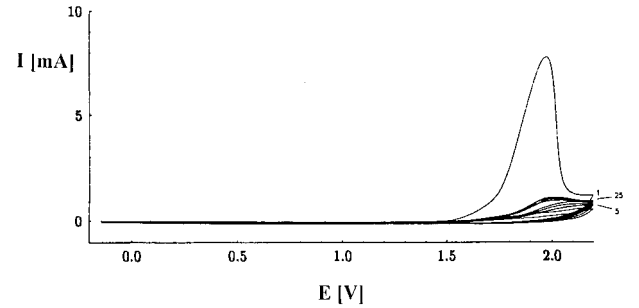


Figure 1. Cyclic voltammogram of trityl ether **3**.

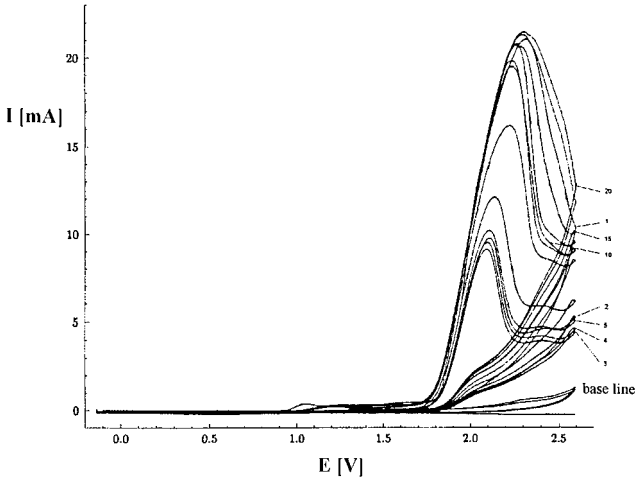


Figure 2. Cyclic voltammogram of benzoate **7**.

depend on their substituents. The dinitrobenzoate **9** showed the lowest oxidation potential at 2.29 V.

To investigate the polymerization of the monomers **2**−**9** the maximum of the oxidation potential was decreased stepwise below the peak potential of the respective monomer to prevent overoxidation. When oxidizing, the ethers **2**−**5** showed a similar behavior to that of the alcohol **1**, as described in the literature.[11] Figure 1 shows a cyclic voltammogram of the trityl ether **3** starting at −0.143 V to a maximum of 2.2 V.

All investigated ethers **2**−**5** showed such characteristic cyclic voltammograms; the anodic peak potentials are listed in Table 1. The peaks shift to lower potentials in the multisweep experiment, their height decreases, and the cyclic voltammogram approximates the base line in the cycles thereafter. No reduction peaks and no visible polymer films were obtained on the electrode. These experiments can be repeated after polishing the anode. No reduction peaks arising from a redoxidizable polymer were observed. From the decreasing current it was concluded that a thin nonconductive film was deposited on the surface of the electrode. These results mean that homopolymerization of the ethers **2**−**5** was unsuccessful. The depositions on the electrode which were formed during the polymerization experiment were nonconductive thin layers without redox properties and with an unknown chemical structure.

The esters **6**−**9** showed another characteristic behavior. In contrast to the case of the investigated ethers, the oxidation current of the cyclic voltammograms did not approximate the base line. In the case of the acetate **6** and the benzoate **7** the oxidation current decreased after the first cycle but increased in the cycles thereafter (see Figure 2 for the benzoate **7**).

The cyclic voltammograms of the esters **8** and **9** showed no decreasing of the oxidation current in contrast to the case for the esters **6** and **7**. These distinctions of the cyclic voltammograms of the esters may be explained by the different chemical character of the protecting groups. Generally, all esters **6**−**9** were continuously oxidized, but there were no reduction peaks in the cyclic voltammograms. At the anode violet streaks were observed in the case of oxidation which disappeared in the reduction phase, but no polymer was deposited. If the potential maximum of the cyclic voltammograms was decreased stepwise below the peak potential of the respective ester, no deposition of a redoxidizable polymer film was observed either. These results mean that the homopolymerization of the esters **6**−**9** was also unsuccessful.

3.3. Copolymerization Experiments. Since no homopolymerization could be achieved, copolymerization was studied. The copolymerization of two different thiophene derivatives is possible, and in some cases functionalized thiophene copolymers can be produced by this way.[7,20,21] In the literature two different mechanisms of the electrochemical polymerization are discussed. The initiation step of the electropolymerization process occurs with the anodic oxidation of a thiophene monomer at the electrode, leading to the formation of a radical cation. Mechanistically the following reaction steps may be possible on the basis of a dimerization of one radical cation with another[22,23] or alternatively the interaction between a radical cation and a neutral monomer molecule,[24,25] demonstrated by the following two pathways:

Formation of radical cations and radical cation dimerization

$$R_1H \rightarrow R_1H^{\bullet+} + e^-$$

$$R_2H \rightarrow R_2H^{\bullet+} + e^-$$

$$R_1H^{\bullet+} + R_2H^{\bullet+} \rightarrow R_1{-}R_2 + 2H^+$$

Formation and interaction of a radical cation with a neutral molecule

$$R_1H \rightarrow R_1H^{\bullet+} + e^-$$

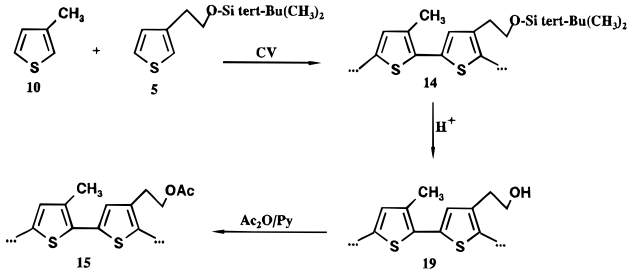
$$R_1H^{\bullet+} + R_2H \rightarrow R_1H{-}R_2H^{\bullet+}$$

$$R_1H{-}R_2H^{\bullet+} \rightarrow R_1{-}R_2 + 2H^+ + e^-$$

The mechanism of the radical cation dimerization is better explained by experiments. According to our experiments we also conclude that the dominant step of the electropolymerization of thiophene derivatives is the radical cation dimerization.[26]

Our copolymerization experiments were carried out with 3-methyltiophene (**10**) with an oxidation potential E_{pox} of 1.94 V, which lies in the same range of the oxidation potentials of the other monomers, and which was successfully copolymerized with thiophene-3-acetic acid.[7] Copolymerization experiments were carried out at a monomer concentration of 0.05 M of both monomers, 3-methylthiophene (**10**) and the respective ether or ester. Cyclic voltammograms started at −0.143 V up to a maximum to oxidize both monomers (for potential ranges see Experimental Section). Copolymerization of **10** with the unprotected hydroxy compound **1** was unsuccessful because **1** prevented the polymer formation and a nonconducting thin film on the surface of the electrode was deposited.[11] The first cycle of the copolymerization experiment of **1** with **10** shows an oxidation peak which shifts to lower voltages in the following

Scheme 3



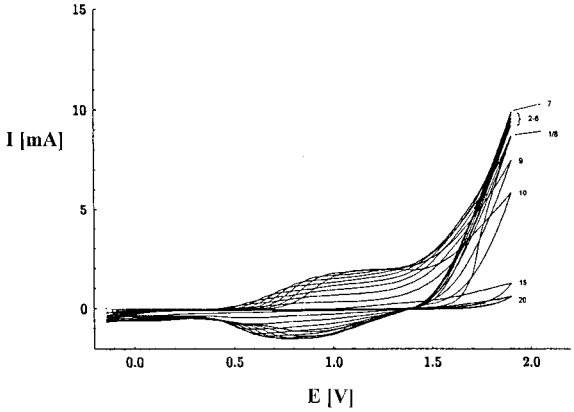


Figure 3. Cyclic voltammogram of the copolymerization of silyl ether **5** with **10** forming copolymer **14**.

cycles; its height decreases, and the cyclic voltammogram approximates the base line.

In the case of the benzyl ether **2** a redoxidizable copolymer **11** was obtained by means of copolymerization with 3-methylthiophene (**10**) which is stable over more than 15 cycles and which could be identified by a FT IR spectrum (ν(C—O ether) 1103 cm^{-1}, for further bands see Experimental Section). The sensitive trimethylsilyl ether **4** showed the lowest copolymerization tendency of the investigated ethers with **10**; only at a potential range of −0.143 to 1.8 V was copolymer deposition possible. From the first to the third cycle the redoxidizable copolymer **13** was formed, identified by the ether band at 1100 cm^{-1} (for further IR bands see Experimental Section). After the third cycle the oxidation current decreased, and with forthcoming cycles the copolymer became nonconducting. The trityl ether **3** showed a higher copolymerization tendency with **10**. At a potential range of −0.143 to 1.9 V copolymer **12** was formed which was stable up to the 6th cycle and could be identified by its FT IR spectrum (ν(C—O ether) 1119 cm^{-1}, for further bands see Experimental Section).

The copolymerization experiment of **10** and the silyl ether **5**, which is more stable against acidic hydrolysis than the ethers **3** and **4**, gave the electroactive copolymer **14**, which was stable up to the 10th cycle (see Scheme 3 and Figure 3) and could be identified by its IR spectrum (ν(C—O ether) 1108 cm^{-1}, for further bands see Experimental Section). After the 10th cycle the oxidation peaks of the monomer and the polymer and the reduction peak of the polymer decreased and slowly approximated the base line. The structure of the polymer was destroyed, and it becomes nonconductive after 25 cycles.

The results of the copolymerization experiments lead to the conclusion that the copolymerization tendency of the ethers **2**−**5** with **10** depends on the stability of the protecting groups against acidic hydrolysis. We suppose that the protons liberated during the electropolymerization[4] can partially cleave the protecting groups to

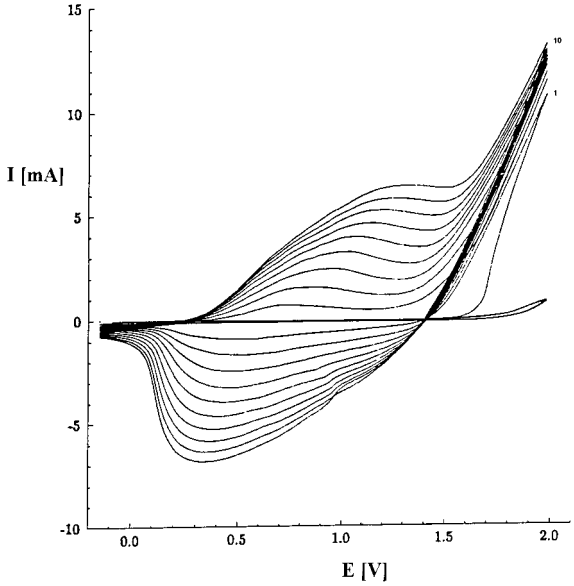


Figure 4. Cyclic voltammogram of the copolymerization of acetate **6** with **10** forming copolymer **15**.

generate the hydroxy compound **1**, which then prevents the copolymerization.

In the case of the copolymerization of **3** and **4** with **10** only a very thin redoxidizable layer was formed, which could only be used for spectroscopic characterization. With increasing cycles no useful material could be produced for further reactions.

The copolymerization of **10** and **5** gave optimal results for further reactions on the surface of the polymer, because redoxidizable layers of **14** could be produced and the protecting ether group could be removed easily by acidic hydrolysis, forming a copolymer with reactive hydroxy groups.

The copolymerization experiments of the esters **6**−**9** succeeded in all cases, leading to stable copolymers with characteristic redox properties. Copolymerization of the acetate **6** and **10** gave the stable and redoxidizable copolymer **15** for 10 and more cycles (see Figure 4) which could be identified by FT IR (ν(C═O acetate) 1743 cm^{-1}, for further bands see Experimental Section). Copolymer **16** (copolymerization of **7** with **10**, ν(C═O benzoate) 1721 cm^{-1}), copolymer **17** (copolymerization of **8** with **10**, ν(C═O *p*-nitrobenzoate) 1727 cm^{-1}), and copolymer **18** (copolymerization of **9** with **10**, ν(C═O 2,5-dinitrobenzoate) 1735 cm^{-1}) were produced in this way. Figure 5 shows the copolymerization of **8** with **10** as an example for these experiments, forming redoxidizable **17** at a potential range of ΔE = −0.143 to 2.1 V.

The cyclic voltammetric studies of the copolymers, washed with acetonitrile and ether to remove monomers and oligomers and dried in vacuo, were carried out in a monomer-free solution of 0.1 M TBAP in acetonitrile at a potential range of −0.143 to 1.4 V. All copolymers showed a stable redox behavior under these conditions; the peak potentials for oxidation E_{pox} and for reduction E_{pred} which are characteristic for the respective copolymers, are listed in Table 2.

In opposition to the case for the monomers the oxidation peaks of the copolymers are much lower. The reduction peaks of the ether copolymers **11**−**14** were measured between 0.97 and 0.80 V. Ester copolymers **15**−**18** showed reduction peaks which are characteristically lower between 0.62 and 0.45 V, possibly influenced by ester substituents.

Figure 6 shows the cyclic voltammogram of the copolymer **16** (resulting from the copolymerization of **7**

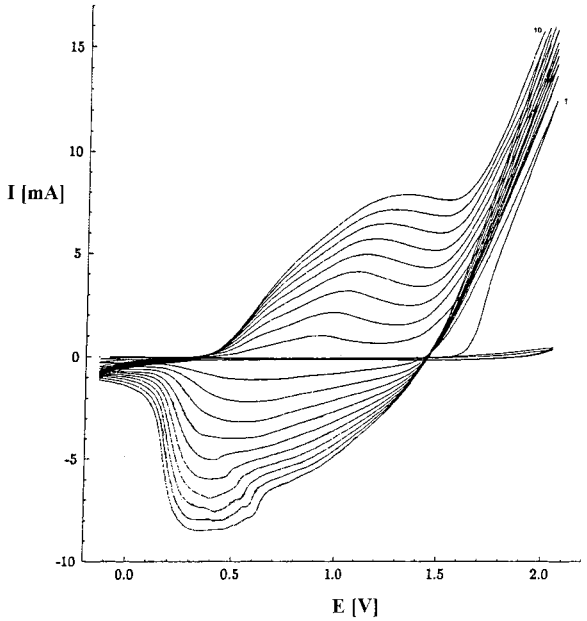


Figure 5. Cyclic voltammogram of the copolymerization of *p*-nitrophenyl benzoate **8** with **10**.

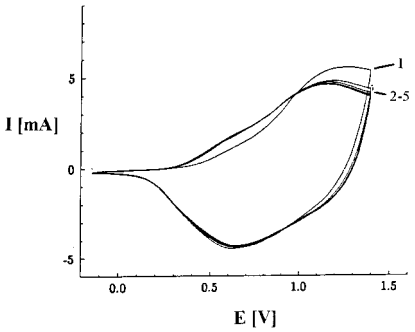


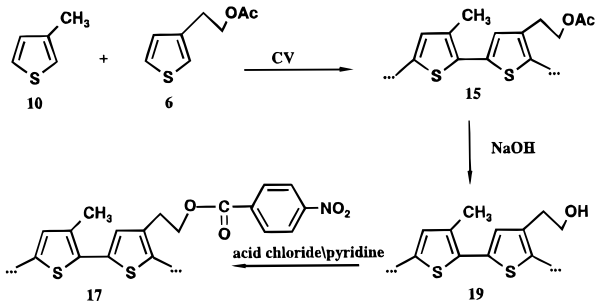
Figure 6. Cyclic voltammogram of the copolymer **16** (1st to 5th cycles).

with **10**) as a typical example. The oxidation potential E_{pox} amounts to 1.18 V, and the reduction potential E_{pred} to 0.62 V. The cyclic voltammogram shows the reversible oxidation and reduction of the copolymer **16**. After five cycles the charge value was measured to be 349 mC for oxidation and 332 mC for reduction.

Determination of the ratio of monomer units of **10** and the respective comonomer in the copolymers was difficult, because the Kubelka Munk spectra of the copolymers did not contain typical IR bands for 3-methylthiophene (**10**) units, which would have been comparable with the characteristic ether bands of **2**−**5** or ester bands of **6**−**9**. Because of the very low quantities of the ether copolymers available by electrocopolymerization, no elemental analyses were possible. Since the ester copolymers **17** and **18** contain nitrogen, the cyclic voltammetric copolymerizations were continued over a long period of time in order to produce a quantity of the copolymer sufficient for elemental analyses. From equimolar quantities of the comonomers the ratio of monomer units of **10** and the comonomer was approximately 4:1 in the case of **17** and 5:1 in the case of **18**, calculated from the nitrogen values of the elemental analyses. The molar ratio of **10** and the comonomers can be modified by differing concentrations of the monomers and by potentiostatic polymerization in order to achieve taylor-made copolymers, as described for a copolymer containing carboxylic groups.[27]

3.4. Reactions of the Polymer Films. In order to prove the activity of the functional groups in the

Scheme 4



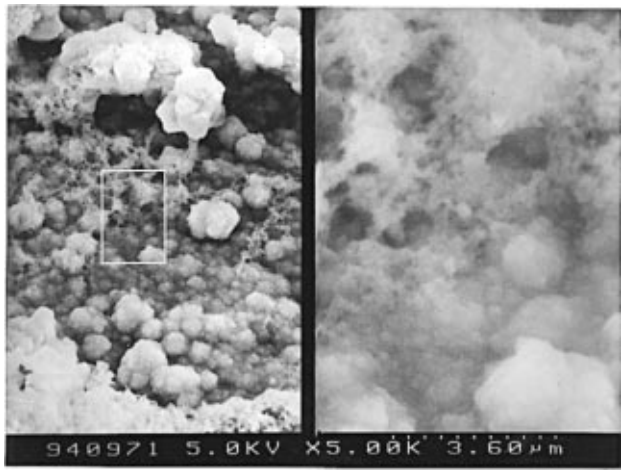


Figure 7. SEM photograph of copolymer **14**, prepared by copolymerization of **5** with **10**.

copolymers, model reactions with the copolymer **14** were carried out to show the reactivity of the hydroxy groups on the surface of the polymeric film (see Scheme 3). The protecting group of **14** was removed by acidic hydrolysis. The resulting copolymer **19** with reactive hydroxy groups was treated with acetic anhydride/pyridine. Acetate groups of the analogously prepared polymer **15** gave characteristic IR bands at 1735 cm^{-1}, identical with the bands found for copolymer **15** synthesized by copolymerization of the acetate **6** with **10** (see Scheme 4). Cleavage of the acetate groups of the copolymer **15** and conversion of the resulting copolymer **19** (ν(OH) 3561 cm^{-1}) with *p*-nitrobenzoyl chloride in pyridine gave copolymer **17**, identified by IR spectroscopy. **17** can also be synthesized by electrochemical copolymerization of **8** with **10**.

Cyclic voltammograms of the copolymers **15**, **17**, and **19**, which were produced by reactions of the corresponding polymer films, characterize their electrochemical behavior (see Table 2). The oxidation peak of the copolymer **19**, which contains reactive hydroxy groups, gave no characteristic maximum. This can be interpreted as an additional oxidation of the hydroxy groups, and the assumption is supported by the results of chemical reactions: The analogous acylation of **19** to the acetate copolymer **15** or to the *p*-nitrobenzoate copolymer **17**, carried out after cyclic voltammetric investigation of **19**, was unsuccessful because of irreversible electrochemical oxidation of the copolymer. Figures 7−9 present typical SEM photographs, which show the characteristic morphology of copolymers produced by cyclic voltammetric experiments.

The surface of copolymer **14** showed a bulby structure with several caves which are also visible at higher magnifications (see Figure 7). In the case of copolymer **15** containing acetoxy groups (see Figure 8) a characteristic spongy structure had developed on the electrode.

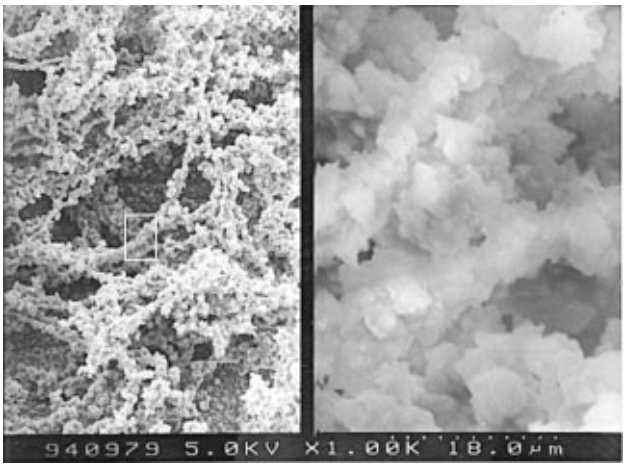


Figure 8. SEM photograph of copolymer **15**, prepared by copolymerization of **6** with **10**.

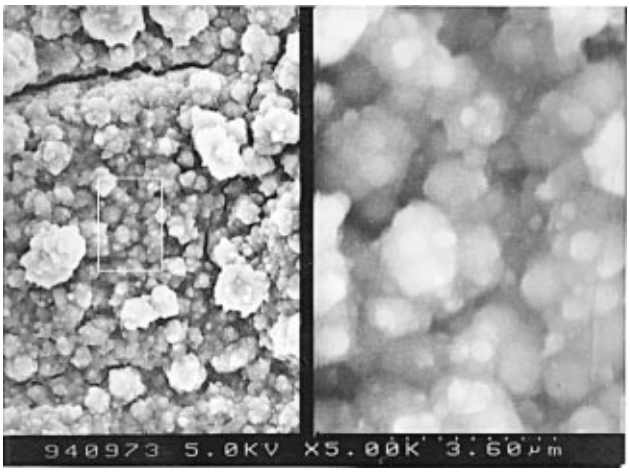


Figure 9. SEM photograph of copolymer **17**, prepared by copolymerization of **8** with **10**.

By higher magnification a relative compact structure can be seen. The surface of copolymer **17** (see Figure 9) possesses an irregular structure with bulby depositions. It can be supposed that such polymer layers, with a thickness of about 0.5 μm, formed during 10 polymerization cycles, and having a rough surface, are suitable carrier materials for enzyme electrodes because of their high number of reactive groups and their large inner surface.

4. Conclusions and Outlook

Thiophene polymers are potential carrier materials for reagents such as enzymes. In order to carry out polymerization and copolymerization experiments, several thiophene derivatives with protected hydroxy groups were synthesized. The hydroxy function can be protected as either an ether or an ester function. Starting from 3-(2-hydroxyethyl)thiophene (**1**), protected thiophene derivatives were synthesized as ethers, 3-(2-(benzyloxy)-ethyl)thiophene (**2**), 3-[2-((triphenylmethyl)oxy)ethyl]-thiophene (**3**), 3-[2-((trimethylsilyl)oxy)ethyl]thiophene (**4**), 3-[2-((dimethyl-*tert*-butylsilyl)oxy)ethyl]thiophene (**5**), and as esters, 3-(2-acetoxyethyl)thiophene (**6**), 3-(2-(benzoyloxy)ethyl)thiophene (**7**), 3-[2-((*p*-nitrobenzoyl)-oxy)ethyl]thiophene (**8**), and 3-[2-((3,5-dinitrobenzoyl)-oxy)ethyl]thiophene (**9**). Electrochemical polymerization of these protected thiophene derivatives was studied under cyclic voltammetric conditions and at various potential ranges. Under the chosen conditions homopolymerization was unsuccessful, but in some cases copolymerization with 3-methylthiophene (**10**) was achieved. The silyl ether **5** as well as the esters **6**−**9** were polymerized successfully, as shown by reflection IR spectra. The morphology of the thiophene copolymers was characterized by SEM photographs. Cyclic voltammetric conditions showed the redox properties of the copolymers in their protected form. Reactions of the polymer film established the reactivity of hydroxy groups on the surface of the copolymer and also showed the covalent incorporation of protected hydroxy functionalized thiophene units in the copolymers. In further investigations, the copolymerization conditions as well as the immobilization reaction with enzymes should be optimized.

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