Synthesis of Functionalized Thiophenes for the Preparation of Conducting Polymer Films with Complexing Properties

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Four series of novel substituted thiophenes (Schiff bases, esters, amides, and amino acids) have been synthesized and tested for their ability to form conducting polymer films via cyclic voltammetry in order to obtain electrochemical sensors for metal cations. The influence of the nature and size of the substituents on the electropolymerizability of the monomers has been studied.

INTRODUCTION

Conducting polythiophenes   have been used for many different applications,[1] such as light emitting devices,[2] capacitors, field-effect transistors,[4] antistatic films,[5] or biosensor components.[6] The introduction of different substituents in the thiophene ring allows large variations of properties of the polymers.[7] However, the size of substituents can significantly influence the process of polymerization and the conductivity of the final polymer chain. Metal coordination to polymer thiophenes or mixed thiophene-containing polymers induces equally significant changes of the properties of the compounds.[8]

   In previous publications, we have shown that silica grafted with complexing groups, such as amino acids or dicarboxylates, are efficient scavengers for divalent metal cations[9] and can be used for the preparation of electrochemical detectors.[10] To assure electrical conductivity, however, they were incorporated into a conducting matrix of carbon paste, which led to sensors of low mechanical stability. If it would be possible to graft the same type of functional groups on a conducting polymer, the conducting matrix would no longer be necessary, and the stability of the device would be largely enhanced.

   With the aim of preparing conducting polythiophenes with ion-complexing properties, we have synthesized thiophene monomers bearing different functional groups at the 3 position of the ring, in order to study their effect on the electron density and consequently on the facility of the electropolymerization of these monomers.

RESULTS AND DISCUSSION
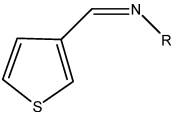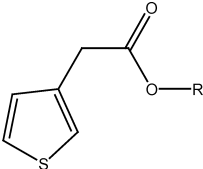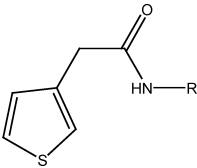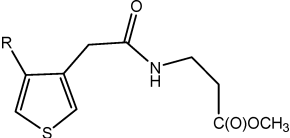
Synthesis of Monomers

In order to introduce complexing groups into the thiophene ring, we have chosen to synthesize Schiff bases, esters, amides, and thiophenyl amino acids, which are presented in Table I. The methods of synthesis are described in detail in the experimental section.

Electropolymerization

For all the monomers synthesized, we have studied their ability to form conducting polymer films on an electrode surface by using the technique of Cyclic Voltammetry (CV). The device used was a classical three-electrode system, the solvent being either acetonitrile or dichloromethane, and tetra-*n*-butylammonium tetrafluoroborate being the inert electrolyte. The measurements have been realized at different

TABLE I Thiophene Monomers

Schiff bases		R	
		n-Pr	**1**
		i-Pr	**2**
		n-Bu	**3**
		n-Hept	**4**
Esters		R	
		Me	**5**
		i-Pr	**6**
		n-Bu	**7**
Amides		R	
		n-Pr	**8**
		i-Pr	**9**
		n-Hept	**10**
Amino acids		R	
		H	**11**
		OCH$_3$	**12**

concentrations of the monomers, different scan rates, and various limits of the oxidation potential.

Typical results are shown in Figures 1–6. It can be seen from Figure 1 that the oxidation of **2** starts at a potential of about 1.1 V, and then the current increases without formation of a visible voltammetric peak. For **3** (Figure 2) the oxidation potential is higher by about 50 mV; in this case, however, the formation of a voltammetric peak at about 1.58 V is clearly visible. Both compounds undergo irreversible oxidation, and the oxidation products do not yield a conducting polymer deposited on the electrode. In both cases a small reduction peak can be observed at about 0.1 V due to the presence of protons removed from these molecules.

The cyclic voltammetry curve for thiophen-3-yl-acetic acid methyl ester **5** is shown in Figure 3. The onset of the monomer oxidation is close to 1.19 V, and with scanning to 2.25 V the current increases rapidly without formation of a peak. However, in the reverse cycle two reduction

FIGURE 1 Cyclic voltammetry of *N*-(3-thienylmethylene)-*i*-propyl-1-amine **2** (0.01 M, black lines) and pure electrolyte (gray lines) in 0.1 M NBu$_4$BF$_4$/ CH$_2$Cl$_2$ solution. Scan rate: 50 mV·s^{-1}.

peaks can be observed at potentials of 0.12 and 1.05 V. The first one, similar to the two compounds previously mentioned is representative of proton reduction, while the second is connected with the reduction of the oxidized polymer forming a layer on the electrode. During the second voltammetric cycle, the polymer oxidation peak is visible at 1.25 V, and for each subsequent cycle, both reduction and oxidation currents increase, indicating the increase of the thickness of the polymer layer. The potential of the oxidation peaks is shifted with every scan toward more positive values, which indicates a moderate conductivity of the
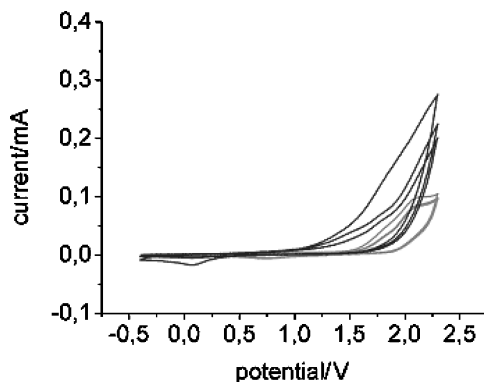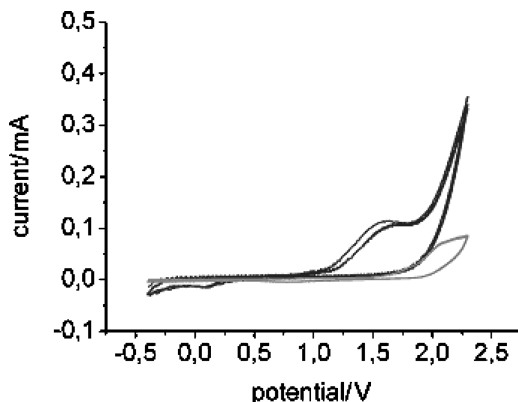

FIGURE 2 Cyclic voltammetry of *N*-(3-thienylmethylene)-*n*-butyl-1-amine **3** (0.01 M, black lines) and pure electrolyte (gray line) in 0.1 M NBu$_4$BF$_4$/ CH$_2$Cl$_2$ solution. Scan rate: 50 mV·s^{-1}.

FIGURE 3 Cyclic voltammetry of thiophen-3-yl-acetic acid methyl ester **5** (0.02 M, black lines) and pure electrolyte (gray line) in 0.1 M NBu_4BF_4/ CH_2Cl_2 solution. Scan rate: 50 mV·s^{-1}.

polymer layers formed. This behavior is similar to that described in the literature for other 3-substituted thiophenes bearing carboxyl groups.[11]

Figure 4 shows cyclic voltammetric curves for thiophen-3-yl-acetic acid *i*-propyl ester **6**. This compound starts to oxidize at very high potentials close to 1.9 V; even in acetonitrile, a solvent that allows extending the oxidation domain up to 2.5 V, only an unclear peak at 2.4 V is observed. The oxidation process is irreversible, and the formation of a conducting polymer at the electrode is not observed.
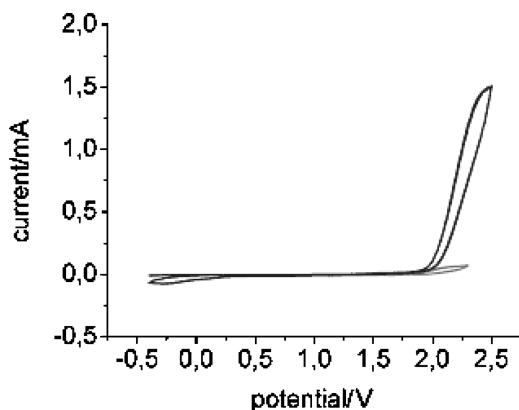
FIGURE 4 Cyclic voltammetry of thiophen-3-yl-acetic acid *i*-propyl ester **6** (0.01 M, black line) and pure electrolyte (gray line) in 0.1 M NBu_4BF_4/ acetonitrile solution. Scan rate: 50 mV·s^{-1}.
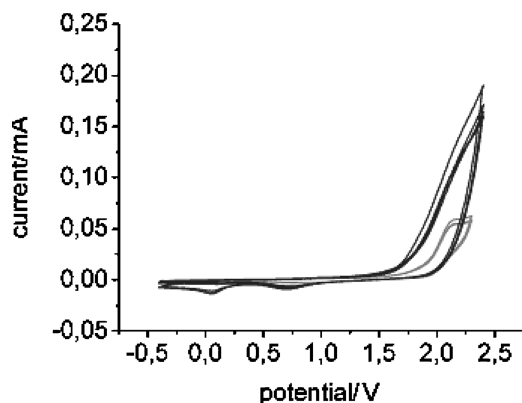
FIGURE 5 Cyclic voltammetry of *N-i*-propyl-2-thiophen-3-yl-acetamide **9** (0.01 M, black lines) and pure electrolyte (gray lines) in 0.1 M NBu_4BF_4/ CH_2Cl_2 solution. Scan rate: 50 mV·s^{-1}.

The results of the electrochemical studies of *N-n*-propyl-2-thiophen-3-yl-acetamide **8** and methyl 3-[(3-thienylacetyl)amino]propanoate **11** are shown in Figures 5 and 6, respectively. The onset of oxidation for both compounds is visible at 1.5–1.8 V, but the process is irreversible. In both cases the formation of conducting polymers is not observed, possibly due to a preferential oxidation of the amide group, as suggested by Koßmehl et al.[12] In the case of **8** two very well-resolved reduction peaks can be observed at about 0.7 and 0.05 V due to the formation of σ-dimers and simultaneous removal of protons from these molecules.
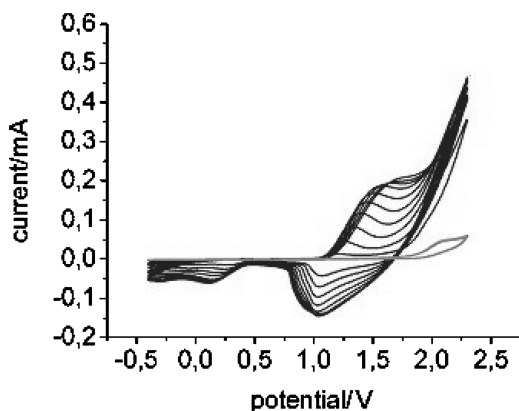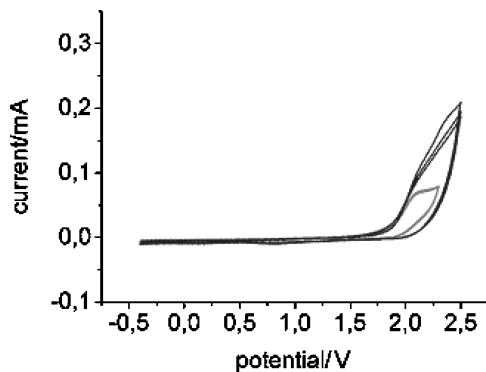

FIGURE 6 Cyclic voltammetry of methyl 3-[(3-thienylacetyl)amino]pro-panoate **11** (0.01 M, black lines) and pure electrolyte (gray line) in 0.1 M NBu_4BF_4/ CH_2Cl_2 solution. Scan rate: 50 mV·s^{-1}.

CONCLUSION

From the figures above it can be seen that only the monomer bearing a relatively small substituent, a methyl ester group, leads to a conducting polymer (Figure 3). The remaining compounds do not form a conducting polymer film on the electrode surface. In this case polymerization may occur, but the macromolecular chains obtained are not sufficiently planar to lead to observable conducting properties.

The fact that among different members of the same series of compounds (e.g., thienyl esters) only the monomer with the least voluminous substituent yields evidence for the formation of a conducting polymer film indicates that the decisive factor for the electropolymerizability is the steric hindrance of bulky substituents and not their electron-withdrawing properties.

A comparison of the different series of monomers indicates that the smallest Schiff base **1** does not form conducting films, whereas methyl ester **5** of similar size allows for polymerization. This may be due to a higher flexibility of the ester with respect to the more rigid Schiff base.

These observations lead to the conclusion that a "dilution" of the substituent density along the macromolecular chain should be in favor of the formation of a planar polythiophene structure and hence a significantly higher conductivity along the chain. This can be obtained by, e.g., using as monomers di- or trimers of thiophene bearing only one complexing function per molecule. Work in this direction is under progress.

EXPERIMENTAL

Experimental Protocols

All solvents were reagent grade and used without further purification. Progress of the reactions and purity of the products were evaluated using thin layer silica gel chromatographic (TLC) plates (Merck, Darmstadt, Germany, Kieselgel 60 F_{254}) with ethyl acetate-hexane mixtures as eluents. Purification was carried out, when necessary, by flash silica gel column chromatography with the same eluents. Melting points were determined with an electronic apparatus (electrothermal) and have not been corrected. ^{1}H NMR spectra were recorded on Bruker DRX 400 or AM 200 spectrometers. Chemical shifts are reported in ppm downfield from internal tetramethylsilane (TMS) and the coupling constants in Hz. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer equipped with an Attenuated Total Reflection (ATR) accessory. Elemental analyses were carried out on a Thermofinnigan FlashEA 1112 apparatus. They agree with the proposed structures, and illustrative results are reported for some compounds.

For the CV experiments, a three-electrode glass cell was used, with a platinum working electrode (0.07 cm^2 surface area), a platinum-wire counter-electrode, and a Ag/Ag$^+$ reference. Potential sweeps were controlled by a CHI 620A potentiostat (CH Instruments, Austin, Texas, USA). Solvents used in these studies were either anhydrous dichloromethane or acetonitrile. Tetra-*n*-butyl ammonium tetrafluoroborate served as an inert electrolyte. The concentrations of thiophenes that were examined varied from 0.005 to 0.1 mol·L^{-1}; optimal results have been obtained in the concentration range of 0.01–0.02 mol·L^{-1}.

Syntheses

Preparation of Schiff Bases

N-*(3-Thienylmethylene)*-n-*propyl-1-amine (1).* In a typical experiment 1 eq. of 3-thiophene carbaldehyde (1.12 g, 10 mmol) was added to 1.2 eq. of *n*-propylamine (0.71 g, 12 mmol) and 0.02 g of *p*-toluene sulfonic acid, dissolved in 50 mL of toluene. The mixture was heated to reflux for 3 h under stirring in a reactor equipped with a Dean-Stark head. After cooling to r.t., the solution was extracted twice with 15 mL of aq. NaHCO$_3$, twice with 15 mL of sat. NaCl, and finally 3 times with 15 mL of water. The organic phase was dried over anhydrous Na$_2$SO$_4$.

After evaporation of the solvent, the product **1** was obtained as a yellow liquid (1.4 g, 92%). Elemental analysis: Found: C, 62.9; H, 7.4; N, 8.9; S, 20.5. Calcd. for C$_8$H$_{11}$NS: C, 62.7; H, 7.2; N, 9.1; S, 20.9. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.1–7.6 (m, 3H, thiophenes-H), 8.28 (s, 1H, N=CH), 3.52 (t, $J = 6.9$ Hz, 2H, CH$_2$-N), 1.70 (m, 2H, CH$_3$C*H*$_2$), 0.94 (m, 3H, CH$_3$). IR ν_{max} (film, cm^{-1}): 1641 (C=N), 780 (monosubstituted thiophene).

The following members of the series have been prepared in an analogous manner.

N-*(3-Thienylmethylene)*-i-*propyl-1-amine (2).* 1.12 g (10 mmol) of 3-thiophene carbaldehyde, 0.78 g (12 mmol) of *i*-propylamine. Yield 0.8 g (52%) of a light yellow oil. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.1–7.7 (m, 3H, thiophenes-H), 8.30 (m, 1H, N=CH), 3.50 (m, 1H, CH−N), 1.31 (d, $J = 6.2$ Hz, 6H, CH$_3$). IR ν_{max} (film, cm^{-1}): 1635 (C=N), 780 (monosubstituted thiophene).

N-*(3-Thienylmethylene)*-n-*butyl-1-amine (3).* 1.12 g (10 mmol) of 3-thiophene carbaldehyde, 0.88 g (12 mmol) of *n*-butylamine. Yield 1.49 g (90%) of a yellow oil. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.2–7.5 (m, 3H, thiophenes-H), 8.19 (m, 1H, N=CH), 3.49 (t, $J = 7.0$ Hz, 2H, CH$_2$−N), 1.61 (m, 2H, CH$_3$CH$_2$C*H*$_2$), 1.31 (m, 2H, CH$_3$C*H*$_2$CH$_2$), 0.88

(t, $J = 7.4$ Hz, 3H, CH$_3$). IR ν_{max} (film, cm^{-1}): 1640 (C=N), 779 (mono-substituted thiophene).

N-*(3-Thienylmethylene)*-n-*heptyl-1-amine (4).* 1.12 g (10 mmol) of 3-thiophene carbaldehyde, 1.38 g (12 mmol) of *n*-heptylamine. Yield 2.07 g (99%) of a dark yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.1–7.6 (m, 3H, thiophene-H), 8.26 (m, 1H, N=CH), 3.55 (t, $J = 7.0$ Hz, 2H, CH$_2$-N), 1.67 (m, 2H, C*H$_2$*CH$_2$N), 1.28 (br m, 8H, CH$_3$(C*H$_2$*)$_4$CH$_2$), 0.89 (t, $J = 6.5$ Hz, 3H, CH$_3$). IR ν_{max} (film, cm^{-1}): 1642 (C=N), 782 (monosubstituted thiophene).

Preparation of Esters

Thiophen-3-yl-acetic Acid Methyl Ester (5). One eq. (1.42 g, 10 mmol) of 3-thiophene acetic acid was dissolved in 100 mL of methanol containing 0.1 g of sulfuric acid as a catalyst. The mixture was refluxed for 6 h. The methanol was removed under reduced pressure. The residue was dissolved in 20 mL of ethyl acetate, and the solution was extracted twice with 15 mL of aq. NaHCO$_3$, twice with 15 mL of sat. NaCl, and finally 3 times with 15 mL of water. The organic phase was dried over anhydrous MgSO$_4$. The product (1.55 g, 99%) was a viscous yellow oil.
Elemental analysis: Found: C, 54.0; H, 5.3; S, 20.2. Calcd. for C$_7$H$_8$O$_2$S: C, 53.8; H, 5.2; S, 20.5. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.0–7.3 (m, 3H, thiophene), 3.65 (s, 2H, CH$_2$), 3.62 (s, 3H, CH$_3$). IR ν_{max}(film, cm^{-1}): 1733 (ester C=O), 762.

Thiophen-3-yl-acetic Acid i-*Propyl Ester (6).* One eq. (1.42 g, 10 mmol) of 3-thiophene acetic acid, 1.2 eq. (0.75 g, 12 mmol) of iso-propanol, and 0.02 g of *p*-toluene sulfonic acid were dissolved in 100 mL of toluene. The mixture was refluxed for 6 h in a Dean-Stark reactor. After cooling to r.t., the solution was extracted twice with 15 mL of aq. NaHCO$_3$, twice with 15 mL of sat. NaCl, and finally 3 times with 15 mL of water. The organic phase was dried over anhydrous MgSO$_4$. After evaporation of the solvent, the product **6** was obtained as a yellow liquid (1.2 g, 61%). ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.0–7.3 (m, 3H, thiophene-H), 3.65 (s, 2H, CH$_2$), 5.00 (septet, $J = 6.2$ Hz, 1H, CH), 1.21 (d, $J = 6.2$ Hz, 6H, CH$_3$). IR ν_{max} (film, cm^{-1}): 1727 (ester C=O), 763.
The ester **7** was obtained in a similar manner.

Thiophen-3-yl-acetic Acid n-*Butyl Ester (7).* One eq. (1.42 g, 10 mmol) of 3-thiophene acetic acid, 1.2 eq. (0.88, 12 mmol) of *n*-butanol. Yield 1.19 g (60%) of an orange-yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.0–7.35 (m, 3H, thiophenes-H), 3.64 (s, 2H, CH$_2$-C(O)), 4.26 (m, 2H, CH$_2$-O), 1.61 (m, 2H, CH$_3$CH$_2$C*H$_2$*), 1.35 (m, 2H, CH$_3$C*H$_2$*CH$_2$), 0.93 (t, $J = 7.2$ Hz, 3H, CH$_3$). IR ν_{max} (film, cm^{-1}): 1730 (ester C=O), 758.

Preparation of Amides

N-n-*Propyl-2-thiophen-3-yl-acetamide   (8).* Equimolar   amounts (typically 10 mmol) of 3-thiophene acetic acid and *n*-propylamine were dissolved under vigorous stirring in a 90:10 methanol-water mixture. After complete dissolution of the reagents, the solvents were evaporated under reduced pressure and the residue was lyophilized in order to eliminate residual water. The resulting ammonium salt was then dissolved in 100 mL of toluene and the solution refluxed for 6 h in a Dean-Stark reactor. After cooling to r.t., the organic solution was extracted twice with 15 mL of aq. $NaHCO_3$, twice with 15 mL of sat. NaCl, and finally 3 times with 15 mL of water. The organic phase was dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure yielded the crude product as a yellowish paste. After purification on a silica-gel column with hexane/ethyl acetate 20:80 as the eluent, the amide was recovered as a slightly yellow solid. Yield: 1.42 g (77%). Elemental analysis. Found: C, 58.7; H, 7.4; N, 7.2; S, 17.1. Calcd. for $C_9H_{13}NO{:}S$ C, 59.0; H, 7.2; N, 7.6; S, 17.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.0–7.4 (m, 3H, thiophenes-H), 3.61 (s, 2H, CH_2-C=O), 6.90 (br s, 1H, NH), 3.24 (m, 2H, $CH_3CH_2CH_2$), 1.41 (m, 2H, $CH_3CH_2CH_2$), 0.95 (m, 3H, CH_3). IR ν_{max}(KBr, cm^{-1}): 1643 (C(O)N), 760.

The following members of the series have been prepared in an analogous manner.

N-i-*Propyl-2-thiophen-3-yl-acetamide (9).* 0.5015 g (8.5 mmol) of *i*-propylamine and 1.21 g (8.5 mmol) of 3-thiophene acetic acid. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.0–7.3 (m, 3H, thiophenes-H), 3.59 (s, 2H, CH_2—C=O), 5.70 (br s, 1H, NH), 3.95 (septet, $J = 7.0$ Hz, 1H, CH), 1.02 (d, $J = 7.0$ Hz, 6H, CH_3). IR ν_{max} (film, cm^{-1}): 1555 (C=O), 1641 (C(O)—N), 759.

N-n-*Heptyl-2-thiophen-3-yl-acetamide (10).* 1.15 g (10 mmol) of *i*-propylamine and 1.42 g (10 mmol) of 3-thiophene acetic acid. Yield: 1.9 g (79%) of a yellow-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.9–7.4 (m, 3H, thiophene-H), 5.44 (br s, 1H, NH), 3.58 (s, 2H, CH_2—C=O), 3.20 (m, 2H, CH_2-N), 1.78 (m, 2H, CH_2CH_2N), 1.42 (m, 2H, $CH_2CH_2CH_2N$), 1.24 (br m, 6H, $CH_3(CH_2)_3$), 0.87 (t, $J = 6.4$ Hz, 3H, CH_3). IR ν_{max}(film, cm^{-1}): 1553 (C=O), 1643 (C—N), 760.

Preparation of Amino Acids

Methyl 3-[(3-Thienylacetyl)amino]propanoate (11) and Methyl 3-{[(4-Methoxy-3-thienyl)acetyl]amino}propanoate (12). These two compounds were prepared in the same manner: 1 eq. (typically 10 mmol)

of the corresponding 3-thiophene acetic acid (R=H or OCH$_3$), 1 eq. of β-alanine methylester, 1 eq. of benzotriazol(tris-dimethylamino) phosphonium hexafluorophosphate as coupling reagent, and 3 eq. of triethylamine were dissolved in 60 mL of acetonitrile. The mixture was stirred at r.t. for 12 h. After evaporation of the solvent, the residue was redissolved in dichloromethane. The organic solution was extracted twice with 30 mL of 2N hydrochloric acid, twice with 30 mL of aq. NaHCO$_3$, twice with 30 mL of sat. NaCl, and finally 3 times with 30 mL of water. After removal of the solvent under vacuum, the crude product was purified on a silica-gel column with a 20:80 hexane/ethyl acetate mixture as the eluent. The final product was obtained under the form of a viscous translucid gel (1.18 g, 52% for **11**, and 1.24 g, 48% for **12**).

11: Elemental analysis: Found: C, 53.3; H, 5.7; N, 5.8; S, 13.6. Calcd. for C$_{10}$H$_{13}$NO$_3$S: C, 52.9; H, 5.8; N, 6.2; S, 14.1. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 6.9–7.4 (m, 3H, thiophenes-H), 3.56 (s, 2H, thiophene-C*H*$_2$-C=O), 6.41 (br s, 1H, NH), 3.46 (t, $J = 6.0$ Hz, 2H, CH$_2$-N), 2.51 (t, $J = 6.0$ Hz, 2H, C*H*$_2$CH$_2$N), 3.65 (s, 3H, OCH$_3$). IR ν_{max} (film, cm^{-1}): 1732(C=O), 1645 (N—C), 762 (monosubstituted thiophene).

12: ^{1}H NMR (400 MHz, CDCl$_3$) δ: 6.1–7.9 (m, 2H, thiophenes-H), 3.81 (s, 3H, OCH$_3$), 3.58 (s, 2H, thiophene-C*H*$_2$-C=O), 7.74 (br s, 1H, NH), 3.54 (t, $J = 6.2$ Hz, 2H, CH$_2$-N), 2.50 (t, $J = 6.2$ Hz, 2H, C*H*$_2$CH$_2$N), 3.57 (s, 3H, C(O)OCH$_3$). IR ν_{max} (film, cm^{-1}): 1732(C=O), 1646 (N—C), 1553 (3,4-disubstituted thiophene).

REFERENCES

[1] See, for example, T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, *Handbook of Conducting Polymers, 2nd ed.* (Marcel Dekker, New York, 1998).

[2] U. Mitschke and P. Bäuerle, *J. Mater. Chem.*, **10,** 1471 (2000).

[3] (a) A. Laforgue, P. Simon, C. Sarrazin, and J.-F. Fauvarque, *J. Power Sources*, **80,** 142 (1999); (b) A. Du Pasquier, A. Laforgue, and P. Simon, *J. Power Sources*, **125,** 95 (2004).

[4] (a) Z. Bao, *Z. Adv. Mater*., **12,** 227 (2000); (b) G. Horowitz, *Z. Adv. Mater*., **10,** 365 (1998).

[5] (a) F. Jonas and J. T. Morrison, *Synth. Met.*, **85,** 1397 (1997); (b) G. Inzelt, M. Pineri, J. W. Schultze, and M. A. Vorotyntsev, *Electrochim. Acta*, **45,** 2403 (2000).

[6] T. Kuwahara, K. Oshima, M. Shimomura, and S. Miyauchi, *Synth. Met.*, **152,** 29 (2005).

[7] A. Czardybon and M. Lapkowski, *Synth. Met.*, **119,** 161 (2001).

[8] (a) L. Trouillet, M. Lapkowski, O. Stephan, and S. Guillerez, *Synth. Met.*, **109,** 277 (2000); (b) S. Guillerez and G. Bidan, *Synth. Met.*, **93,** 123 (1998).

[9] (a) F. Hamdoune, C. El Moujahid, M.-J. Stébé, C. Gérardin, P. Tekely, C. Selve, et al., (b) *Progress in Colloid and Polymer Science,* **118,** 107 (2001); F. Hamdoune, C. El Moujahid, L. Rodehüser, C. Gérardin, B. Henry, M.-J. Stébé, et al., *New J. Chem.*, **24,** 1037 (2000).

[10] S. Sayen, C. Gérardin, L. Rodehüser, and A. Walcarius, *Electroanalysis*, **15,** 422 (2003).

[11] (a) J. Dai, J. L. Sellers, and R. E. Noftle, *Synth. Met*., **139,** 81 (2003); (b) S. J. Howell, C. S. Day, and R. E. Noftle, *Inorg. Chim. Acta*, **358,** 3711 (2005).

[12] G. Li, G. Koßmehl, H.-P. Welzel, W. Plieth, and H. Zhu, *Macromol. Chem. Phys*., **199,** 2737 (1998).