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Tetrahedron

Tetrahedron 62 (2006) 758-764

Development in synthesis and electrochemical properties of thienyl derivatives of carbazole

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Received 10 March 2005; revised 12 September 2005; accepted 29 September 2005

Available online 4 November 2005

Abstract—A convenient and higher yielding synthetic route to *N*-alkyl-bis(thiophene)- and *N*-alkyl-bis(ethylenedioxythiophene) carbazole derivatives is reported and their aggregation, and electrochemical properties are characterized. The key step in the synthesis of this group of compounds has been the Stille-type coupling reaction between the *N*-alkyldibromocarbazole and tin derivatives of thiophene or ethylenedioxythiophene, as the best way for preparation of conjugated *N*-alkylcarbazole derivatives. For this group of compounds we also present an electrochemical polymerization effect.

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1. Introduction

Since their discovery, conjugated monomers and their polymers attract continuing interest as a result of their suitability in a broad range of applications, such as batteries,¹ electroluminescent devices, field-effect transistors and photovoltaics.

The need for sensitive and highly specific chemical sensors is of growing importance in both the monitoring and control of human exposure to chemicals present in environment and medical technology. As a result of this great hopes and expectations are associated with sensors based on organic materials. The manufacture of high quality ultrathin, anisotropic organic films by means of the Langmuir– Blodgett (LB) technique is finding important practical application in many fields including sensorics, electrooptics and electronic devices as well as biomimetic systems.^{1–7}

Carbazole is a well-known hole-transporting and electroluminescent unit. Polymers containing carbazole moieties either in the main or side chains have attracted much attention because of their unique properties, which allow for various photonic applications (photoconductivity, electroluminescence, and photorefraction).^{8,9}

In this paper, supplementing our previous publications, we report on the synthesis of novel amphiphilic, monomeric derivatives of 2-thiophene- and 2-(3,4-ethylenedioxythiophene)carbazole, and their aggregation properties in LB films.^{10–12} In many photonic applications like photon funnels or energy transfer controllers¹³ the concentration of chromophore is essential as well as the knowledge of the LB film architecture. We undertook the study of formation of single and two-component Langmuir and LB films of synthesized alkylheteroaromatic molecules. Particular attention has been paid to the films containing alkylheteroaromatic compounds mixed with polyoctadecylthiophene (PODT), docosanoic acid (DA) and 22-tricosenoic acid (TA), which are low molecular mass amphiphilic molecules facilitating the deposition (DFs-Deposition Facilitators). PODT was prepared by the typical chemical oxidative polymerisation with FeCl₃, DA and TA (Aldrich) were carefully recrystallised from chloroform.

Since the Langmuir–Blodgett technique allows the controlled, layer-by-layer deposition of ordered molecular films on solid substrates, the films constructed by means of this method are expected to be components for potential applications in sensorics, photonics or photoelectronics.¹⁴

Advantages in the processability of chemically polymerized soluble thiophene derivatives, have been recognized by a number of researchers in this field. But chemical polymerization enables the deposition of films on substrates by a variety of methods, for example the Langmuir–Blodgett technique. In this case electrochemical deposition of polymer on platinum or ITO plates were used. The photophysical properties of the thin film of monomers

Keywords: Electrochemical properties; Thienyl derivative; Carbazole.

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and polymers and their electrochemical properties were then investigated.

2. Results and discussion

2.1. Synthesis of bis(2-thiophene)- and bis(2-(3,4-ethylenedioxythiophene))carbazoles

Based of our previous work,¹⁵ we found that the Stille procedure is a convenient method for the preparation of another group of carbazole derivatives with aggregation properties. One of them, *N*-nonyl-3,6-bis(2-thiophene)carbazole (TPC, **3c**) was patented because of its gave aggregation and electrochemical properties.¹⁶

Scheme 1 illustrates the synthetic routes for the novel *N*-alkyl-3,6-bis(2-thiophene)- or -(2-(3,4-ethylenedioxy-thiophene))carbazoles. These compounds were synthesized by a two-step procedure. *N*-alkylcarbazole (1)¹⁷ was successfully brominated using *N*-bromosuccinimide (NBS), to give the dibromo compound **2**. A Stille-type coupling reaction was employed to obtain 3,6-bis (2-thiophene)-*N*-alkylcarbazole (**3**) from 2-trimethyltinthiophene (Scheme 1) and 3,6-dibromo-*N*-alkyl-carbazole (**2**). A similar procedure was used to synthesize the 2-(3,4-

Scheme 1.

ethylenedioxythiophene) derivatives of N-alkylcarbazoles (4). Compound 4 was achieved with a high yield (90%) using this method.

The structures of the synthesized compounds were confirmed by ¹H and ¹³C NMR, and elemental analysis.

2.2. Langmuir films

The molecular structures of the components for the binary systems of interest are shown in Figure 1.

To obtain Langmuir films, the synthesized compounds (Scheme 1): *N*-butyl-3,6-bis(2-thiophene)carbazole (**3a**), *N*-butyl-3,6-bis(2-(3,4-ethylenedioxythiophene)carbazole (**4a**), *N*-amyl-3,6-bis(2-thiophene)carbazole (**3b**), *N*-amyl-3,6-bis(2-(3,4-ethylenedioxythiophene)carbazole (**4b**), *N*-nonyl-3,6-bis(2-thiophene)carbazole (**3c**), *N*-decyl-3,6-bis(2-thiophene)carbazole (**3d**), *N*-decyl-3,6-bis(2-thiophene)carbazole (**3d**), *N*-decyl-3,6-bis(2-thiophene)carbazole (**4d**), were dissolved in chloroform (Aldrich, HPLC grade). Concentrations of solutions were maintained at ca. 1 mg/ml.

The films of desired composition were formed by dropwise spreading of *N*-alkylcarbazole derivatives solutions, with or without DFs (docosanoic acid, tricosenoic acid and



Figure 1. The binary system components: 3c, N-nonyl-3,6-bis(2-thiophene)carbazole (TPC); 4a, N-butyl-3,6-bis(2 (3,4-ethylenedioxythiophene) carbazole (DTPC); 5, PODT; 6, TA; 7, DA.

polyoctadecylthiophene) on high purity water at 295 K. The binary systems were mixed to obtain resulting molar compositions of the deposition mixture of 2:1, 1:1 and 1:2. The electrical conductivity of this quartz double distilled, deionized water was lower than 10^{-5} S/m. The π -A isotherms were measured by means of a commercial LB trough (KSV, System 5000), using a Pt hydrophilic Wilhelmy plate. The compression rates used in our experiments ranged between 5 and 100 mm/min, depending on the rigidity of the films. From the measured π -A isotherms of all synthesized derivatives of *N*-alkylcarbazole it was clear that the derivatives with an even number of C atoms in alkyl chains do not form stable Langmuir films.¹⁸ Therefore N-nonyl-3,6-bis(2-thiophene)carbazole (TPC)the derivative with odd number of C atoms in the alkyl chains was chosen for further experiments. Properties of the other derivatives are still under investigation. Figure 3 shows the π -A isotherms of the investigated binary systems of TPC. For comparison the π -A isotherm of pure TPC is shown in Figure 2. Although pure TPC forms good Langmuir films their LB films are not very stable because the transfer occurs under a relatively low surface pressure. The surface pressure π is generally considered to be equal to the reduction of the pure liquid surface tension by the film, i.e. $\pi = \sigma_0 - \sigma$, where σ_0 is the surface tension of the pure liquid and σ is the tension of the film covered surface.



Figure 2. π -A Isotherm of TPC.

Comparison of π -A isotherms of Figure 3 shows that when using binary films, one can obtain much higher surface pressures and therefore closer packing, and PODT facilitates this process the most effectively. This is caused by synergy between the structures of TPC and PODT.



Figure 3. π -A Isotherms of TPC-DA, TPC-PODT, TPC-TA complexes.



Figure 4. The computer-generated models of TPC.

In Figure 4 a computer-generated (optimization structure-AM1, *Gaussian*03, Molekel) model of the TPC molecule is presented. If the average plane of all aromatic rings (hydrophilic part of molecule) was laid flat on the water, the aliphatic chain would be elevated by 35° . In such an arrangement calculated area per molecule equals ca. 1.1 nm^2 , which is also confirmed by π -A isotherm.

During compression, molecules can slip each under the other forming a 'spoon like' stacking and in close packed phase (liquid condensed) both calculated and measured, from π -A isotherm, the area per molecule amounts to ca. 0.4 nm². In Figure 5 we propose LB film structures for the binary systems of interest. Tricosenoic and docosanoic acids, the model amphiphiles can also be effectively used for creation of binary systems of interest.



Figure 5. LB films structures of measured binary systems.

In our case the deposited LB films are complete and of high quality, as confirmed by additivity of UV–vis spectra (Fig. 6).

Contrary to TPC, DTPC does not form any stable Langmuir films, neither alone nor in binary systems. In solution it forms dimers, as confirmed by 2D photoluminescence spectra. The 2D photoluminescence spectrum together with excitation and emission spectra are shown in Figure 7.

In the excitation spectrum of DTPC (Fig. 7) one can observe two strong, specific regions, a monomer region (ca. 330 nm), and one corresponding to the dimer (ca. 400 nm). In the emission spectrum, the monomer region is at a characteristic wavelength at ca. 380 nm whereas the second region (470 nm) is covered by the absorbance of the dimer.



Figure 6. UV-vis spectra of binary complex's (TPC-PODT) LB films.



Figure 7. 2D Photoluminescence spectrum of DTPC.

2.3. Electrochemical characterization of PTPC

To enable a comparison of the conductivity of LB films in different binary systems, electrochemically deposited poly(*N*-nonyl-3,6-bis(thiophene)carbazole) (PTPC) films were generated. The electrochemical synthesis of PTPC was carried out by the galvanostatic method on both platinum and ITO-coated glass substrates.

At Figure 8 is shown the repeated potential scan polymerization for TPC in 0.1 M tetrabuthylammonium perchlorate/acetonitrile. The polymerization begins at an $E_{\text{onset,m}}$ of 0.09 V with an $E_{\text{p,m}}$ at 0.15 V. Carbazoles electropolymerize at much lower potential and relative rapidly compared to the single-ring monomers such as pyrrole, or EDOT.



Figure 8. Repeating potential scanning polymerization of 0.01 mol TPC in 0.1 M tetrabutylammonium perchlorate/acetonitrile (TBAP/CH₃CN) at a scan rate of 100 mV/s.

The preferred method of polymer synthesis for optimum film formation was the application of potential near 1.4 V in an electrolyte solution of $(Bu)_4N(BF_4)$ 0.2 M/acetonitrile. The deposition of PTPC was found to proceed rapidly and the synthesis of thick PTPC films was not complicated and we were able to obtain homogenous and stable electroconductive polymer (σ =6.25×10⁻⁸ S/cm).

Figure 9 shows the conductivity dependence as a current–voltage plot, which is linear over the range of film thickness.



Figure 9. Current-voltage characteristic of electropolymer PTPC.

In our case we were only able to measure the spectroelectrochemistry of an electrochemically prepared film of PTPC (Fig. 10). The absorption spectra of solutions of PTPC were not obtained, due to the insoluble nature of the polymer.

The absorbance spectrum of the thin PTPC layer suggests a ground state electronic structure with minimal interchain aggregation in the condensed state.¹⁹

The dark PTPC polymer is illustrated by the photograph in Figure 11.

From our previous experience and theoretical calculations²⁰ we can say that the structure of TPC should be almost planar, whereas the dihedral angle between the central ring (carbazole) and lateral one (thiophene) is 27.5° (Fig. 12).



Figure 10. The UV-vis spectrum of electropolymer PTPC film.



Figure 11. PTPC polymer films electrochemical deposited on ITO glass after electrical measurements.



Figure 12. Fully optimized geometries (AM1 level of theory) of *N*-nonyl-3,6-bis(2-thiophene)carbazole, TPC.

3. Conclusions

A series of *N*-alkylcarbazole derivatives have been synthesized using the Stille condensation reaction. This methodology provides a convenient route to obtain the title compounds, which could find applications for example in sensoric and active materials.²¹ Carbazole derivatives mixed with substances facilitating film building gave stable and good quality Langmuir and Langmuir–Blodgett films of desired composition. We examined the electroconductivity of LB films built with TPC monomer in a binary system. The electrical properties of a thin polymer film of PTPC, obtained by electrochemical polymerization, were determined.

4. Experimental

4.1. General

Melting points are uncorrected. All NMR spectra were acquired a Brucker VXR-300 at 300 (^1H) and 75 (^{13}C) MHz

in CDCl₃ using TMS as internal standard. Column chromatography was carried out on Merck Kiesel silica gel 60. Dry DMF was used immediately after distilling from a solution containing benzophenone-sodium. Other starting materials, reagents and solvents were used as received from suppliers.

The purity of the products was checked by thin layer chromatography, and their molecular structures were confirmed by ¹H NMR and ¹³C NMR spectroscopy as well as by elemental analysis and UV–vis spectroscopy.

4.2. Synthesis

4.2.1. Compound a. *The procedure for preparation of N-alkylcarbazoles* (**1a–1d**). *N*-Alkylation of aromatic compounds involving nitrogen heterocycles such as carbazole with alkyl halide in presence of based solution and benzyl triethyl ammonium chloride (BTEAC) as phase-transfer catalyst readily proceeded under mild conditions, starting from 1 g of carbazole.¹⁷

Selected data for 1c. Y=81% (1.41 g), mp 23–24 °C, ¹H NMR (CDCl₃) δ 8.10 (d, J=7.8 Hz, 2H, arom. H), 7.49–7.37 (m, 4H, arom. H), 7.25–7.19 (m, 2H, arom. H), 4.27 (t, J=7.2 Hz, 2H, CH₂), 1.84 (q, J=7.2 Hz, 2H, CH₂), 1.46–1.24 (m, 12H, CH₂), 0.87 (t, J=7.2 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 140.4, 140.0, 125.7, 123.0, 120.5, 118.8, 108.8, 43.1, 32.0, 29.6, 29.6, 29.4, 29.3, 29.1, 27.4, 22.8, 14.4. For C₂₁H₂₇N calcd C, 85.95; H, 9.27; N, 4.77, found; C, 85.70, H, 9.05, N, 4.67.

4.2.2. Compound b. *The procedure for preparation of N-alkyl-3,6-dibromocarbazole* (**2a–2d**). *N*-Alkylcarbazoles were converted to dibromocarbazole derivatives in presence of NBS in anhydrous chloroform, starting from 1 g of **1a–1d**.¹⁷ *Selected data for* **2b**. *Y*=78% (1.30 g), mp 72 °C, ¹H NMR (CDCl₃) δ 8.04 (s, 2H, arom. H), 7.47 (d, *J*=9.1 Hz, 2H, arom. H), 7.16 (d, *J*=10.1 Hz, 2H, arom. H), 4.15 (t, *J*=7.2 Hz, 2H, CH₂), 1.75 (q, *J*=7.2 Hz, 2H, CH₂), 1.30–1.20 (m, 4H, CH₂), 0.79 (t, *J*=6.8 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 139.3, 129.0, 123.4, 123.3, 111.9, 110.4, 43.3, 29.3, 28.6, 22.5, 13.9. For C₁₇H₁₉N calcd C, 86.02; H, 6.80; N, 5.90, found; C, 85.9; H, 6.75; N, 5.79.

Compound **2c**. Y=83% (1.28 g), mp 46–47 °C, ¹H NMR (CDCl₃) δ 8.06 (s, 2H, arom. H), 7.48 (d, J=6.7 Hz, 2H,arom. H) 7.19 (d, J=8.6 Hz, 2H, arom. H), 4.15 (t, J=7.2 Hz, 2H, CH₂), 1.76 (q J=7.1 Hz, 2H, CH₂), 1.25–1.17 (m, 12H, arom. H), 0.82 (t, J=6.5 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 139.3, 129.0, 123.4, 123.2, 111.9, 110,4, 43.3, 31.8, 29.4, 29.3, 29.2, 28.7, 27.2, 22.6, 14.1. For C₂₁H₂₅NBr₂ calcd C, 55.89; H, 5.58; N, 3.10, found; C, 55.76; H, 5.48; N, 3.00.

Compound **2d.** Y=81% (1.23 g), mp 54–56 °C, ¹H NMR (CDCl₃) δ 8.14 (s, 2H, arom. H), 7.56 (d, J=6.7 Hz, 2H, arom. H), 7.27 (d, J=8.7 Hz, arom. H), 4.45 (t, J=7.0 Hz, 2H, CH₂), 1.81 (q, J=7.1 Hz, 2H, CH₂), 1.35–1.19 (m, 14H, CH₂), 0.91 (t, J=6.8 Hz, 3H, CH₃). ¹³C NMR δ 140.5, 125.6, 122.9, 120.4, 118.8, 108.7, 43.1, 31.9, 29.6, 29.6, 29.4, 29.0, 27.4, 22.8, 14.3. For C₂₂H₂₇NBr₂ calcd C, 56.78; H, 5.85; N, 3.015, found; C, 56.70; H, 5.75; N, 2.95.

4.2.3. Compound c. *The procedure for preparation of N-alkyl-3,6-(2-thiophene)carbazoles* (**3a–3d**). Monomers were synthesized according to our previous method¹⁵ by a coupling reaction of *N*-alkyl-2,7-dibromocarbazoles (**2a–2d**) with 2-trimethyltin-thiophene, starting from 1 g of **2a–2d**. *Selected data for* **3a**. *Y*=78% (0.79 g), mp 110 °C, ¹H NMR (CDCl₃) δ 8.35 (d, *J*=7.1 Hz, 2H, arom. H), 7.75 (d, *J*=10.3 Hz, 2H, thioph. H), 7.41–7.37 (m, 4H, arom, H), 7.27 (d, *J*=7.2 Hz, 2H, thioph. H), 7.13 (d, *J*=6.4 Hz, 2H, thioph. H), 4.30 (t, *J*=7.2 Hz, 2H, CH₂), 1.90–1.66 (m, 2H, CH₂), 1.64–1.32 (m, 4H, CH₂), 0.95 (t, *J*=7.3 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 140.4, 125.5, 122.8, 120.3, 118.6, 108.6, 42.7, 31.1. 20.5, 13.8. For C₂₄H₂₁NS₂ calcd C, 74.38; H, 5.46; N, 3.61; found C, 74.60; H, 5.68; N, 3.20.

Compound **3b.** Y=75% (0.76 g), mp 63 °C, ¹H NMR (CDCl₃) δ 8.05 (s, 2H, arom. H), 7.49 (d, J=6.8 Hz, 2H, arom. H), 7.31–7.29 (m, 2H, arom. H), 7.19–7.16 (m, 4H, arom. H), 7.09–7.07 (m, 2H, arom.H), 4.13 (t, J=7.2 Hz, 2H, CH₂), 1.75 (q, J=7.4 Hz, 2H, CH₂), 1.46–1.22 (m, 4H, CH₂), 0.82 (t, J=6.9 Hz, 3H, CH₃). ¹³C NMR, (CDCl₃) δ 139.3, 129.0, 126.9, 125.2, 123.5, 123.3, 111.9, 110.4, 43.3, 29.4, 28.6, 22.5, 13.9. For C₂₅H₂₃NS₂ calcd C, 74.80; H, 5.77; N, 3.49; found C, 74.40; H, 5.20; N, 3.30.

Compound **3c**. Y=80% (0.81 g), mp 193–195 °C, ¹H NMR (CDCl₃) δ 8.05 (s, 2H, arom. H), 7.47 (d, J=6.8 Hz, 2H, arom. H), 7.32–7.29 (m, 2H, arom. H), 7.17 (d, J=8.7 Hz, 2H, arom. H), 7.09–7.07 (m, 2H, arom. H), 4.13 (t, J=7.2 Hz, 2H, CH₂), 1.75 (q J=7.1 Hz, 2H, CH₂), 1.25–1.19 (m, 12H, CH₂), 0.81 (t, J=6.8 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 139.3, 126.9, 125.1, 123.5, 123.3, 111.9, 110.4, 43.4, 31.9, 29.5, 29.3, 28.8, 27.2, 22.7, 14.1. For C₂₉H₃₁NS₂ calcd C, 76.13; H, 6.83; N, 3.06; found C, 75.90; H, 6.50; N, 2.88.

Compound **3d.** Y=76% (0.77 g), mp 189–191 °C, ¹H NMR (CDCl₃) δ 8.05 (s, 2H, arom. H), 7.48 (d, J=6.8 Hz, 2H, arom. H), 7.32–7.29 (, 2H, arom. H), 7.18 (d, J=8.7 Hz, 2H, arom. H), 7.09–7.07 (m, 2H, arom. H), 4.13 (t, J=7.2 Hz, 2H, CH₂), 1.75 (q, J=7.1 Hz, 2H, CH₂), 1.25–1.16 (m, 14H, CH₂), 0.84 (t, J=6.8 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 139.3, 129.0, 126.9, 125.1, 123.4, 123.3, 111.9, 110.4, 43.4, 31.9, 29.5, 29.3, 29.2, 28.8, 27.2, 22.6, 14.1. For C₃₀H₃₃NS₂ calcd C, 76.41; H, 7.05; N, 2.97; found C, 76.35; H, 6.95; N, 2.70.

4.2.4. Compound d. *The preparation of N-alkyl-3,6-(2-(3,4-ethylenedioxythiophene))carbazoles* (**4a–4b**). These compounds were successfully synthesized according to our method reported for preparation of 3,4-ethylenedioxythiophene derivatives of tetrazines, starting from 1 g of **2a–2d**.¹⁵

Compound **4a**. Y=90% (1.19 g), oil, ¹H NMR (CDCl₃) δ 8.02 (s, 2H, arom. H), 7.46 (d, J=6.7 Hz, 2H, arom. H), 7.17 (d, J=8.7 Hz, 2H, arom. H), 6.26 (s, 2H, arom. H), 4.12 (t, J=7.2 Hz, 10H, CH₂), 1.72 (q, J=7.4 Hz, 2H, CH₂), 1.27 (sec., J=7.5 Hz, 2H, CH₂), 0.87 (t, J=7.3 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 141.8, 139.3, 129.0, 123.4, 123.2, 111.9, 110.6, 110.4, 99.7, 64.7, 43.0, 31.0, 20.5, 13.9. For C₂₈H₂₅NS₂O₄ calcd C, 66.77; H, 5.00; N, 2.78, found C, 66.20; H, 4.60; N, 2.70.

Compound **4b**. Y = 88% (1.15 g), mp 68–70 °C, ¹H NMR (CDCl₃) δ 8.02 (s, 2H, arom. H), 7.46 (d, J = 6.7 Hz, 2H,

arom. H), 7.15 (d, J=8.7 Hz, 2H, arom. H), 6.3 (s, 2H, arom. H), 4.13 (m, 10H, CH₂), 1.73 (q, J=7.2 Hz, 2H, CH₂), 1.28–1.21 (m, 4H, CH₂), 0.81 (t, J=6.8 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 141.8, 139.3, 129.0, 123.4, 123.2, 111.9, 110.4, 99.7, 64.7, 43.3, 29.4, 28.6, 22.5, 13.9. For C₂₉H₂₇NS₂O₄ calcd C, 67.23; H, 5.26; N, 2.71 found C, 66.89; H, 4.66; N, 2.67.

Compound **4c**. Y=91% (1.16 g), oil, ¹H NMR (CDCl₃) δ 8.04 (s, 2H, arom, H), 7.46 (d, J=6.8 Hz, 2H, arom. H), 7.16 (d, J=8.7 Hz, 2H, arom. H), 6.25 (s, 2H, arom. H), 4.12 (t, J=7.2 Hz, 10H, CH₂), 1.73 (t, J=7.0 Hz, 2H, CH₂), 1.24–1.17 (m, 14H, CH₂), 0.81 (t, J=6.8 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 141.8, 139.3, 129.0, 123.5, 123.2, 111.9, 110.4, 99.7, 64.7, 43.4, 31.8, 29.4, 29.3, 29.2, 28.8, 27.2, 22.6, 14.1. For C₃₃H₃₅NS₂O₄ calcd C, 69.08; H, 6.15; N, 2.44 found C, 68.70; H, 5.73; N, 2.04.

Compound **4d**. Y=89% (1.12 g), mp 55 °C, ¹H NMR (CDCl₃) δ 8.05 (s, 2H, arom. H), 7.47 (d, J=6.8 Hz, 2H, arom. H), 7.18 (d, J=8.7 Hz, 2H, arom. H), 6.26 (s, 2H, arom. H), 4.13 (t, J=7.2 Hz, 2H, CH₂), 1.74 (q, J=7.1 Hz, 2H, CH₂), 1.24–1.16 (m, 14H, CH₂), 0.81 (t, J=6.8 Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ 141.8, 139.3, 129.0, 1253.5, 123.3, 111.9, 110.4, 99.7, 64.7, 43.4, 31.9, 29.5, 29.4, 29.3, 29.2, 28.8, 27.2, 26.7, 14.1. For C₃₄H₃₇NS₂O₄ calcd C, 69.49; H, 6.35; N, 2.38; found, C, 69.30; H, 6.20; N, 2.27.

4.3. Oxidative polymerization

Monomer TPC was electrochemically polymerized using repeated potential scan polymerization with a standard three-electrode. Electropolymerization of TPC was carried on in 0.1 M tetrabuthylammonium perchlorate/acetonitrile at a scan rate of 100 mV/s.

4.4. Electrochemical polymerization

Polymer electrochemistry was carried out on a standard model galvanostat employing a platinum disk working electrode or ITO (area = 1.55 cm²) disk working electrode, and a platinum plate counter electrode. Spectroelectrochemistry experiments were carried out on a Cary 100 Bio Varian UV–vis spectrophotometer. Polymer films were deposited onto ITO-coated glass plates ($9.8 \times 50.0 \times 0.5$ mm, $20 \ \Omega$ /square, Delta Technologies). Insoluble polymers were cast onto ITO or platinum plates ($10 \times 70 \times 0.2$ mm) from dry acetonitrile.

Acknowledgements

Financial support from the Polish Science Foundation (KBN, Grant No. PBZ-KBN-098/T09/2003) is gratefully acknowledged.

References and notes

- 1. Nguyen, V. C.; Potje-Kamloth, K. *Thin Solid Films* **1999**, *338*, 142–148.
- Cabala, R.; Meister, V.; Potje-Kamloth, K. J. Chem. Soc., Faraday Trans. 1997, 93, 131–137.

- 3. Selampinar, F.; Toppare, L.; Akbulut, U.; Yalcin, T.; Süzer, S. *Synth. Met.* **1995**, *68*, 109–116.
- 4. Toppare, L.; Akbulut, U.; Yalçin, T.; Süzer, S. Synth. Met. **1995**, 68, 109–116.
- 5. Brook, T. E.; Narayanaswamy, R. Sensors Actuators B 1998, 51, 77–83.
- 6. Swager, T. M. Acc. Chem. Res., 1998, 31, 201-207.
- 7. Iraqi, A.; Wataru, I. Chem. Mater. 2004, 16, 442-448.
- Sanda, F.; Nakai, T.; Kobayashi, N.; Masuda, K. *Macromole*cules 2004, 37, 2703–2708.
- Mello, S. V.; Dynarowicz-Łętka, P.; Dhanabalan, A.; Bianchi, R. F.; Onmori, R.; Janssen, R. A. J.; Oliveira, O. N., Jr. *Colloid. Surf. A* 2002, 198–200, 45–51.
- Chyla, A.; Kucharski, S.; Janik, R.; Sworakowski, J.; Bieńkowski, M. *Thin Solid Films* **1996**, 284–285, 496–499.
- Chyla, A.; Lewandowska, A.; Sołoducho, J.; Górecka-Drzazga, A.; Szablewski, M. *IEEE. Trans. DEI* 2001, *8*, 559–565.

- Niski, H.; Kohno, H.; Kano, T. Bull. Chem. Soc. 1981, 54, 1897–1898.
- 13. Langmuir–Blodgett Films; Roberts, G. G., Ed.; Plenum Press: New York, 1990.
- 14. Bard, A. J. Integrated Chemical Systems. A Chemical Approach to Nanotechnology; Wiley: New York, 1994.
- Sołoducho, J.; Doskocz, J.; Cabaj. Roszak, S. *Tetrahedron* 2003, 59, 4761–4766.
- 16. Sołoducho, J.; Cabaj, J.; Chyla, A. Pol. Pat. 2004, P369, 384.
- Sotzing, G. A.; Reddinger, J. L.; Katritzky, A. R.; Sołoducho, J.; Musgrave, R.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1997**, *9*, 1578–1587.
- 18. Jarvis, N. L. J. Phys. Chem., 1965, 69, 1789.
- Chama, M.; Myles, D. J. T.; Hicks, R. G. Chem. Mater. 2005, 17, 2672–2678.
- Sołoducho, J.; Roszak, S.; Chyla, A. New J. Chem. 2001, 25, 1175–1181.
- 21. Chevrot, C.; Henri, T. Synth. Met. 2001, 118, 157-166.