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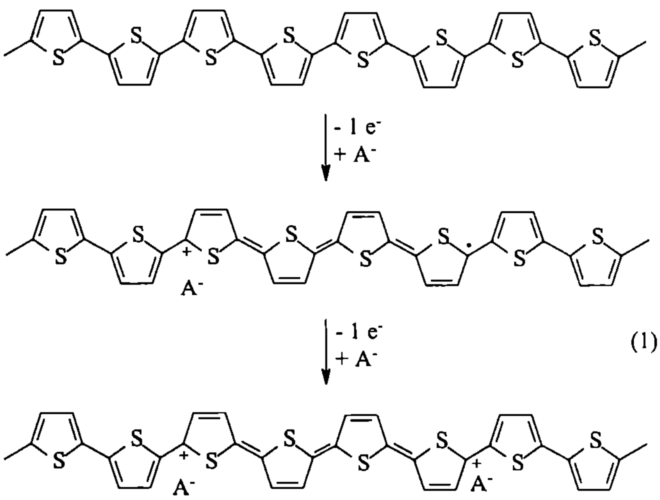
Synthesis and spectroscopic characterization of polythiophenes containing pendant oligoaniline groups

Summary — We report on a new class of hybrid conjugated polymers in which side oligoaniline groups are attached to the poly(2,5-thienylene) main chain. Soluble polymers of this type can be obtained by copolymerization of 3-alkylthiophene with thiophene functionalized at the position 3 with oligoanilines (aniline dimer and aniline tetramer). The resulting polymers are electroactive and may be electrochemically doped *via* anodic oxidation similarly as classical polythiophenes. In addition their side oligoaniline chains can be selectively doped *via* protonation (doping of acid-base type). Spectroscopic properties of undoped polymers as well as spectroscopic consequences of the doping process are discussed in details. Poly(3-alkylthiophene-*co*-3-oligoanilinethiophene)s are promising materials for the fabrication of polymeric solar cells since in addition to their electron donating properties their absorption spectrum covers a large range of the visible spectrum.

Key words: poly(3-alkylthiophenes), aniline oligomers, doping, copolymers, electrochemistry, spectroelectrochemistry.

Polyanilines and polythiophenes constitute the most extensively studied families of conductive polymers mainly due to their easy processibility and good environmental stability. One should however note that their chemical and electrochemical characteristics are distinctly different. Polythiophenes, for example, are conductive by a redox type of doping in which neutral polymer chains are transformed into polycarbonium cations. Simultaneously charge compensating anions (dopants) are inserted into the polymer matrix [equation (1)] (see for example [1]). In the case of polyanilines this doping can be of a redox nature as in polythiophenes [equation (2)], but also of an acid-base nature. The latter takes place if the semi-oxidized form of polyaniline — so called "emeraldine base" — is doped *via* protonation [equation (3)] [1] or *via* complexation with Lewis acids [2].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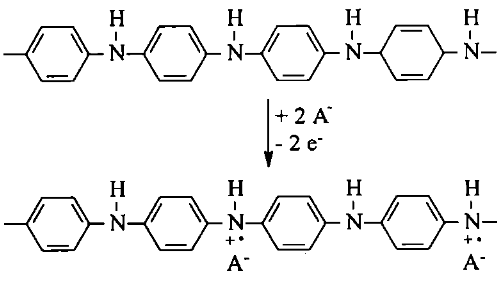
It seems to us interesting to synthesize a hybrid polymer combining the properties of both homopolymers described above, *i.e.* polythiophene and polyaniline. Such new polymers should not only exhibit new and interesting electrochemical and spectroelectrochemical properties but also, in their undoped state, can be considered as excellent candidates for the fabrication of semiconducting layers in "polymeric solar cells". This is due to two principal reasons. First, such hybrid polymers should be good electron donors and good *p*-type con-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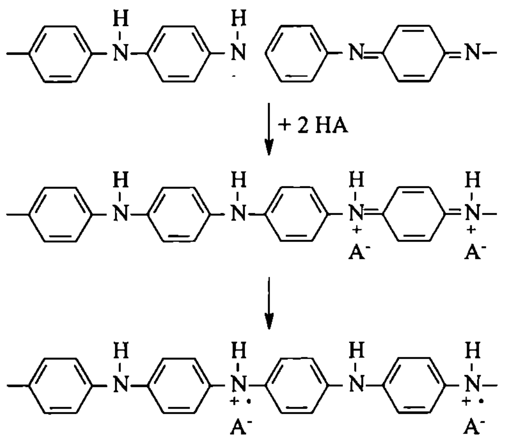

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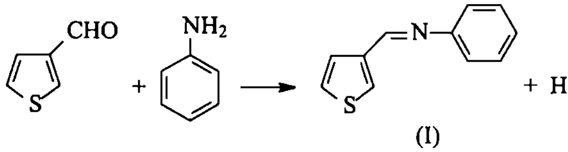
ductors, which facilitates the creation of excitons and their effective dissociation provided that a good electron acceptor is also present in the semiconducting layer. Second, their absorption spectra cover a large range of solar spectrum.

In this paper we describe the synthesis and basic spectroscopic properties of such polythiophenes containing pendant oligoaniline groups.

EXPERIMENTAL

Materials and synthesis of monomers

Three monomers synthesized in this research (1), (2) and (3) are respectively depicted by formula (I), (II) and (III) [see equations (4)—(6)]. Monomer (1), *N*-(thien-3-yl-methylene)-aniline, was obtained from 3-thiophenecarboxyaldehyde and aniline in one-step condensation reaction [equation (4)] by the method similar to described before [3]. Both the aldehyde (Aldrich) and aniline (Aldrich) were purified by vacuum distillation. In a typical reaction procedure 2 g of 3-thiophenecarboxyaldehyde was placed into the reaction vessel equipped with a dropping funnel and reflux condenser. Then 1.66 g of aniline was slowly added drop-wise. During this procedure the temperature of the reaction mixture increased due to exothermic nature of the condensation reaction. The mixture was stirred for additional 2 h, then the product was extracted with diethyl ether, dried over $MgSO_4$ and vacuum distilled using a rotary oven.



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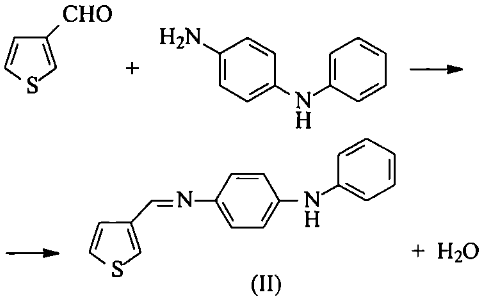
Analytical calculation for $C_{11}H_9NS$: % C = 70.59, % H = 4.81, % N = 7.49, % S = 17.11. Found: % C = 70.26, % H = 4.88, % N = 7.45, % S = 16.25.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.24 (*m*, 3H), 7.38 (*m*, 3H), 7.73 (*m*, 1H), 7.82 (*m*, 1H), 8.46 (*s*, 1H).

IR (KBr, cm^{-1}): 3089 (*m*), 3030 (*w*), 1622 (*s*), 1590 (*s*), 1523 (*w*), 1484 (*s*), 1449 (*w*), 1423 (*w*), 1342 (*w*), 1238 (*m*), 1211 (*m*), 1152 (*m*), 1073 (*m*), 1024 (*w*), 969 (*w*), 905 (*w*), 869 (*m*), 851 (*m*), 826 (*w*), 788 (*s*), 764 (*m*), 724 (*m*), 693 (*s*), 625 (*s*), 543 (*w*), 531 (*w*).

Monomer (2), *N*-phenyl-*N*′-thien-3-ylmethylene-benzene-1,4-diamine, was synthesized in a direct reaction between N-phenyl-1,4-phenylenediamine (Aldrich, used as received) and 3-thiophenecarboxyaldehyde [equation (5)]. First 1.01 g of the aldehyde was dissolved in 100 mL of anhydrous ethanol and placed into the reaction vessel. A solution obtained by dissolving of 1.4 g of *N*-phenyl-1,4-phenylenediamine in anhydrous ethanol was then added drop-wise with constant stirring. The reaction was carried out at 50°C for 2 h. Then the reaction mixture was cooled and kept overnight at room temperature. During that time the crystals of the product precipitated. They were then separated and recrystallized from ethanol two additional times.



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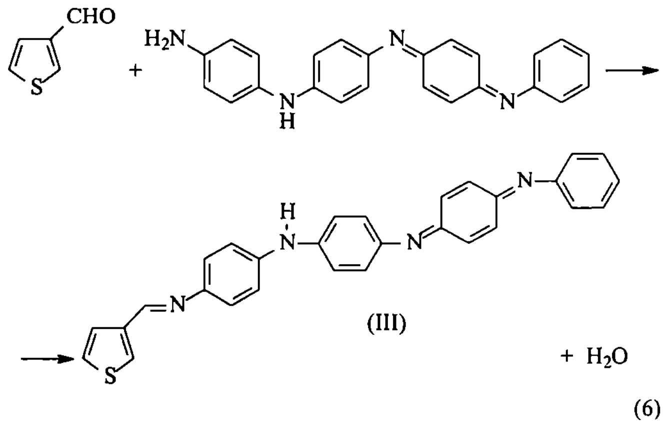
Analytical calculation for $C_{17}H_{14}N_2S$: % C = 73.38, % H = 5.03, % N = 10.07, % S = 11.52. Found: % C = 73.41, % H = 5.13, % N = 9.98, % S = 11.59.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 5.76 (*s*, 1H), 6.94 (*m*, 1H), 7.05—7.35 (*m*, 8H), 7.38 (*m*, 1H), 7.70 (*m*, 1H), 7.78 (*m*, 1H), 8.51 (*s*, 1H).

IR (KBR, cm^{-1}): 3293 (*m*), 3183 (*w*), 3099 (*w*), 3028 (*w*), 1620 (shoulder) (*m*), 1598 (*s*), 1521 (*m*), 1494 (*s*), 1411 (*w*), 1322 (*s*), 1245 (*w*), 1171 (*w*), 1152 (*w*), 1073 (*w*), 1025 (*w*), 959 (*w*), 878 (*w*), 855 (*m*), 830 (*m*), 782 (*m*), 743 (*m*), 715 (*w*), 690 (*w*), 620 (*w*), 532 (*w*).

Monomer (3), *N*-(4-phenylaminophenyl)-*N*′-(4-thien-3-ylmethyleneaminophenyl)-benzene-1,4-diamine, was synthesized from aniline tetramer and 3-thiophenecarboxyaldehyde [equation (6)]. Aniline tetramer, in the



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oxidation state of emeraldine base (4EB), which is not commercially available, was prepared using the method described in details in [4]. Typically 1.0 g of aniline tetramer was first dissolved in 500 mL of anhydrous alcohol and then 0.6 g of 3-thiophenecarboxyaldehyde was added. The reaction mixture was refluxed overnight. The insoluble part of the reaction mixture was separated by filtration and the filtrate was then vacuum pumped in order to remove the solvent and other volatile components of the reaction mixture. Finally the product was washed with large amounts of water and pumped again till constant mass.

Analytical calculation for $C_{29}H_{22}N_4S \cdot 0.5H_2O$: % C = 74.49, % H = 4.96, % N = 11.98, % S = 6.85. Found: % C = 74.30, % H = 4.96, % N = 11.96, % S = 5.76.

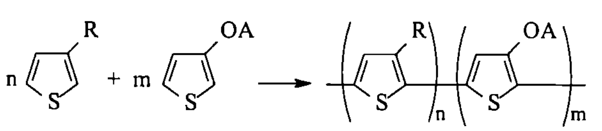
^{1}H NMR (DMSO d6, 200 MHz, ppm): 8.59 (*m*, 1H), 8.44, 8.13, 8.06 (1H), 7.59 (*m*, 2H), 7.4—6.6 (*m*, 17H).

IR (KBr, cm^{-1}): 3381 (*w*), 3289 (*w*), 3193 (*w*), 3083 (*w*), 3027 (*w*), 1615 (*m*), 1590 (*s*), 1510 (*m*), 1495, 1315 (*s*), 1238 (*w*), 1212 (*w*), 1168 (*m*), 1104 (*w*), 1074 (*w*), 955 (*w*), 833 (*m*), 787 (*w*), 748 (*w*), 693 (*w*), 623 (*w*).

IR spectra of the monomers (1)—(3) clearly indicate the presence of -CH=N- functional groups in these compounds. Bands in the range of 1615—1625 cm^{-1}, characteristic for azomethine-type linkages, are present in the reaction products whereas they do not exist in the spectra of the substrates. ^{1}H NMR spectrum of the monomer (3) is significantly more complex than those of the monomers (1) and (2) due to positional isomerism in the tetramer unit [5, 6].

Synthesis of the copolymers

All three monomers tested, although being electrochemically active, do not electropolymerize, probably due to the steric reasons. Monomers (2) and (3) can be however chemically copolymerized with 3-alkylthiophenes [equation (7)] using $FeCl_3$ as an oxidant, according to the modified Sugimoto method [7], to give polymers (P2A, P2B, P3) containing oligoaniline units as pendant groups.



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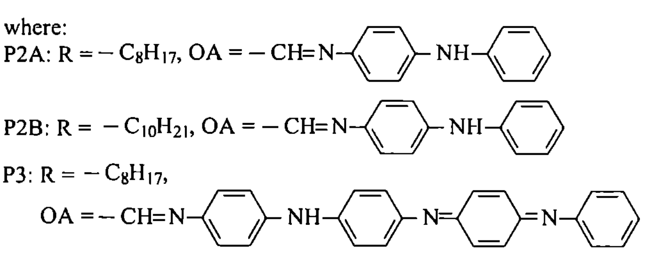

Polymer P3 was obtained from 3-octylthiophene and the monomer (3). Typically both comonomers were dissolved in 50:50 mixture of dried $CHCl_3$ and CH_3NO_2. Then $FeCl_3$ dissolved in the same mixed solvent was slowly added. During the course of the reaction only minimal amount of the insoluble fraction was formed. This fraction was separated by centrifugation and the remaining amount of the copolymer was precipitated with methanol, then repeatedly washed with methanol. Polymerization of thiophenes using iron chloride always leads to partially oxidized (doped) product. Following the recommendation given in [8] the dedoping was achieved by the treatment of the crude polymer with 0.1 M NH_3 solution (repeated three times), which was then completed by a treatment with ammonium salt of ethylenediaminetetraacetic acid (EDTA). The molar ratio of the comonomers (3):3-octylthiophene was 1:8. The following amounts of the reagents were used: 1.376 g of 3-octylthiophene and 0.400 g of the monomer (3) were dissolved in 160 mL of $CHC1_3/CH_3NO_2$ 50:50 mixed solvent, 6 g of $FeCl_3$ was dissolved in 80 mL of the same mixed solvent.

Very similar procedure was used for the preparation of the polymer P2A. However in this case the polymer did not precipitate upon the addition of methanol. In the next step all solvents were therefore evaporated in a rotary evaporator and the remaining solid was repeatedly washed with methanol-water mixture. It was then dedoped in 0.1 M NH_3 solution and dried. The following amounts of the reagents were used: 0.30 g of (2) and 0.69 g of 3-octylthiophene (molar ratio 1:3) were dissolved in the solvent consisting of 45 mL $CHC1_3$ and 35 mL of CH_3NO_2, 2.90 g of $FeCl_3$ were dissolved in 40 mL of $CHC1_3/CH_3NO_2$ 50:50 mixed solvent.

Alternatively P2A was prepared from the monomer (2) and the corresponding 3-octylthiophene *via* oxidation with $FeCl_3$ in pure $CHC1_3$ solvent. Again, as in the previous case, the copolymer could not be precipitated upon the addition of methanol. The solvents were therefore removed using a rotary evaporator. The remaining solid was washed with methanol, then dedoped in 0.1 M NH_3 solution and dried. The amount of reagents were as follows: 0.100 g of the monomer (2) and 0.148 g of 3-octylthiophene (molar ratio 1:2) were dissolved in 6.5 mL of $CHC1_3$. 0.7 g of $FeCl_3$ was dissolved in 14 mL of $CHC1_3$.

The polymer P2B was prepared from the monomer (2) and 3-decylthiophene in pure $CHC1_3$. In this case however small amount of polymer precipitated upon the addition of methanol. This fraction was not further investigated because it contained very little oligoaniline substituent as evidenced by elemental analysis and UV-VIS-NIR spectrum, which closely resembled that of poly(3-octylthiophene). After separation of the fraction precipitated with methanol, the reaction mixture was transferred to a rotary evaporator. The solvents were evaporated and the remaining solid was repeatedly washed with methanol, then dedoped in 0.1 M NH_3 solution and dried. The amounts of reagents were as follows: 0.064 g of the monomer (2) and 0.103 g of 3-decylthiophene (molar ratio 1:2) were dissolved in 10 mL of $CHCl_3$, 0.478 g of $FeCl_3$ was dissolved in 7 mL of $CHCl_3$.

Methods of characterization

For FTIR investigations thin solid films of the polymers P3, P2A and P2B were deposited on the surface of KBr pressed pellet by casting from chloroform solutions.

The same solutions were used for the deposition of thin films of the polymers on a platinum electrode for cyclic voltammetry studies. Cyclic voltammetry curves were registered in 0.1 M Bu_4NBF_4 solution in acetonitrile using platinum working as counter electrode and Ag/AgCl as reference one.

For UV-VIS-NIR spectroelectrochemical investigations the polymers were deposited on an indium-tin oxide (ITO) transparent electrode. Both the counter electrode and the reference one as well as the electrolyte were the same as in the case of the cyclic voltammetry studies. The spectra were recorded in a Perkin-Elmer Lambda 2 spectrometer.

RESULTS AND DISCUSSION

The trials of the preparation of a soluble polymer *via* copolymerization of the monomer (1) with 3-alkylthiophene gave negative results. In this case the only soluble reaction product is the poly(alkylthiophene) homopolymer as evidenced by elemental analysis, which show an absence or negligible amount of N. Moreover spectral features of this fraction are typical for poly(3-alkylthiophene).

However the monomers (2) and (3) do copolymerize with 3-alkylthiophenes to give soluble hybrid conjugated systems (P2A, P2B and P3). Soluble fractions of P2A are enriched in 3-octyl-2,5-thienylene units in comparison with the composition of the reaction mixture. For the ratio of the monomer (2) and 3-octylthiophene equal 1:3 in the reaction mixture, the elemental analysis of the soluble polymer gives the formula $[(3\text{-OT})_{11}(3\text{-DAT})]_n$, where 3-OT denotes 3-octyl-2,5-thienylene unit and 3-DAT denotes 2,5-thienylene unit containing aniline dimer. Similarly for the ratio of the monomer (2) and 3-decylthiophene equal 1:2 in the reaction mixture, elemental analysis of soluble P2B gives the formula $[(3\text{-DT})_6(3\text{-DAT})]_n$, where 3-DT denotes 3-decyl-2,5-thienylene unit. Soluble fraction of P3 [the ratio of (3) and 3-octylthiophene equal 1:8 in the reaction mixture], after the removal of low molecular weight oligomers gives the formula of $[(3\text{-OT})_{13}(3\text{-TAT})]_n$, where 3-TAT denotes 2,5-thienylene unit containing aniline tetramer.

The presence of oligoaniline side group in P2A is also seen in FT-IR spectrum of this polymer (see Fig. 1). The bands at 1601 cm^{-1}, 1502 cm^{-1}, 1310 cm^{-1} and 1166 cm^{-1} can be attributed to the oligoaniline substituent whereas the bands in the spectral range 2950—2850 cm^{-1} together with those observed at 1465 cm^{-1}, 1377 cm^{-1}, 838 cm^{-1} and 721 cm^{-1} are typical for 3-alkyl substituted 2,5-thienylene chain. P2B and P3 give very similar FT-IR spectra.

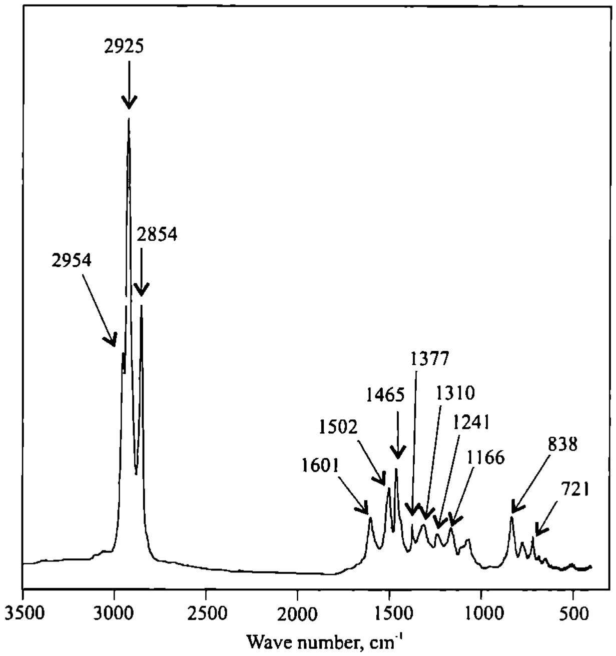

Fig. 1. FT-IR spectrum of copolymer P2B

Since oligoanilines and especially aniline tetramer are strong chromophores, their bonding to the poly(alkylthiophene) chain should give rise of the new absorption bands appearing in the spectral region characteristic for visible radiation (Fig. 2). In P3 spectrum three ab-

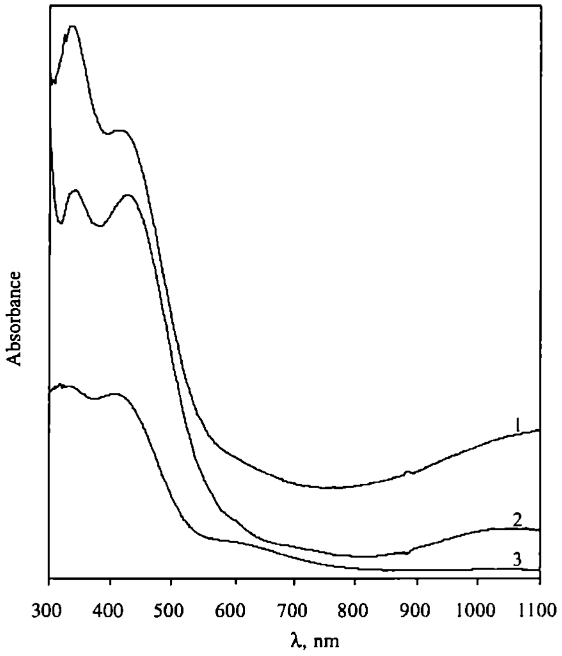

Fig. 2. UV-VIS-NIR absorption spectra of copolymers: 1 — P2A, 2 — P2B, 3 — P3

sorption bands are present (curve 3). The first one at 330 nm is ascribed to π—π* transition in the benzoid ring of the tetramer substituent. One should note that this band is red shifted by *ca.* 15 nm in comparison with the analogous band in "free" aniline tetramer, which is not connected to the poly(2,5-thienylene) chain. This shift can be interpreted as a result of the conjugation of the tetramer π system with that of the poly(2,5-thienylene) main chain *via* the azomethine group. The least energetic band in the range of 570—580 nm is due to excitonic type transition in the oxidized (quinoid type) structural unit of the tetramer substituent. Thus it requires the presence of imine nitrogen and is not observed in totally reduced forms of oligoanilines [9]. It strongly overlaps with the band at 430 nm, which is characteristic for π—π* transition in the 2,5-thienylene unit of the main chain. This band is significantly blue shifted as compared with the analogous band in poly(3-octylthiophene) homopolymer prepared in the same experimental conditions. This blue shift indicates that bonding of oligoaniline pendant groups decreases the conjugation length in the poly(2,5-thienylene) main chain. In the spectra of the polymers P2A (curve 1) and P2B (curve 2) the bands due to π— π* transition in the dimer substituents are present, however the excitonic bands do not virtually exist.

Spectroelectrochemistry is a very convenient method for the investigation of the doping of conductive polymers, especially if combined with cyclic voltammetry. A typical cyclic voltammogram of P2B is presented in Fig. 3. In the potential range studied two broad strongly overlapping anodic peaks can be distinguished, corresponding to the polymer doping, together with their cathodic counterpart peak attributed to the dedoping of the previously doped polymer. One should note here that P2B contains two types of oxidizable (dopable) species: the aniline dimers and the poly(2,5-thienylene) main chain. The former are being oxidized to radical cations, the latter to spinless dications consistent with eq. (1) and eq. (2).

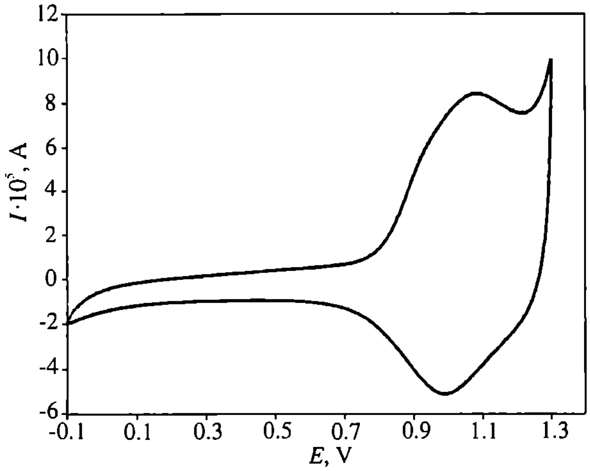

Fig. 3. Cyclic voltammograms of copolymer P2B, scan rate 50 mV/s

The question to be answered is whether these two oxidation processes are sequential or simultaneous. This problem cannot be solved using cyclic voltammetry as a sole research tool. For this reason we have undertaken UV-VIS-NIR spectroelectrochemical studies.

Spectral consequences of the doping process are clearly visible in Fig. 4 where absorption spectra of P2B recorded at different anodic potentials are shown. In accordance with the cyclic voltammogram no oxidative doping is observed for potentials lower than 0.65 V. At E = 0.65 V the onset of the doping is shown by an increase in the absorbance in the range of 700—800 nm, which is characteristic for the doped state of the polymer chain. Simultaneously the bands typical for the neutral polymer start to decrease in the intensity. Further increase in the electrode potential results in a gradual decrease in the peaks at 330 nm and 430 nm and an increase in the doping induced broad absorption band in the range of 700—800 nm. One should also notice that the peak at 330 nm (π—π* transition in the benzoid ring of the substituent) does not disappear totally at high potentials. This is consistent with the postulated oxidation mechanism in which the amine group is oxidized to a radical cation with the aromatic character of the terminal phenyl ring kept. However, due to the fact that increasing electrode polarization induces spectral changes in both oxidizable chromophores — aniline dimer and thienylene chains, nothing can be stated about the sequence of the oxidation processes.

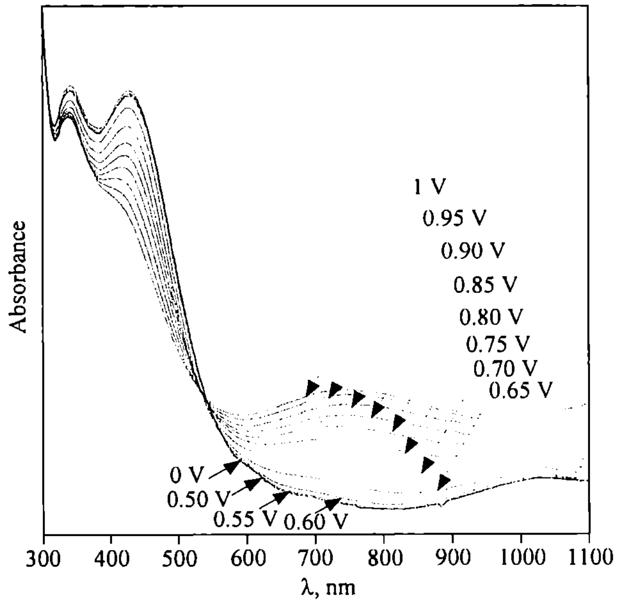

Fig. 4. UV-VIS-NIR absorption spectra copolymer P2B registered at different potentials in Bu_4NBF_4/acetonitrile solution

The polymer P3 shows similar spectroelectrochemical behavior, however its oxidative doping starts at slightly lower potentials (E = 0.55 V). In this case we were able to determine the sequence of dopings using Raman spectroelectrochemistry with infrared excitation line (λ_{exc} = 1064 nm) [4]. It appeared that the doping starts by the oxidation of oligoaniline side groups to radical cations and then is completed by the oxidation of the main thienylene chain to spinless dications (bipolarons).

CONCLUSIONS

We have synthesized, by copolymerization of 3-oligoanilinethiophenes with 3-alkylthiophenes, a new family of hybrid conjugated polymers combining spectroscopic and spectroelectrochemical properties of polyaniline and polythiophene. These new polyconjugated systems are excellent candidates for the fabrication of polymeric solar cells.

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REFERENCES

1. Proń P., Rannou P.: *Prog. Polym. Sci.* 2002, **27**, 135.
2. Kulszewicz-Bajer I., Proń A., Abramowicz J., Jeandey C., Oddou J.-L., Sobczak J.: *Chem. Mater.* 1999, **11**, 552.
3. Inhof W.: *J. Organomet. Chem.* 1997, **533**, 31.
4. Dufour B., Rannou P., Travers J. P., Proń A., Zagórska M., Korc G., Kulszewicz-Bajer I., Quillard S., Lefrant S.: *Macromolecules* 2002, **35**, 6112.
5. MacDiarmid A. G., Zhou Y., Feng J., Furot G. T., Sheldon A. M.: *Polym. Prepr.* 1999, **40**, 246.
6. MacDiarmid A. G., Zhou Y., Feng J.: *Synth. Met.* 1999, **100**, 131.
7. Sugimoto R., Takeda S., Gu H. B., Yoshimo K.: *Chem. Express* 1986, **1**, 635.
8. Andersson M. R., Selse D., Berggren M., Jarvinen H., Hjertberg T., Inganäs O., Wennerström O., Österholm J.-E.: *Macromolecules* 1994, **27**, 6503.
9. Boyer M. I., Quillard S., Cochet M., Louarn G., Lefrant S.: *Electrochim. Acta* 1999, **44**, 1981.