Polish J. Chem., **78**, 1533–1541 (2004)

Synthesis, Electrochemical and Spectroelectrochemical Properties of Viologen Derivative of PEDOT*

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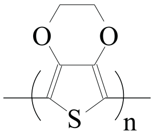
(Received April 15th, 2004; revised manuscript June14th, 2004)

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a highly conductive, low band gap (1.6 eV) polymer. In the oxidized state, thin films of PEDOT are stable and nearly transparent. We present here a derivative of EDOT, a new compound, 1-methyl-1′(6-(2,3-dihydrothieno[3,4-b][1,4]-dioxine-2-yl-methoxy)-hexyl)-4,4′-bipyridylium bis(hexafluorophosphorane). During electro-polymerization it forms a polymer combining good electrochemical and electrical properties of PEDOT with redox and electrochromic properties of viologen. The monomer was also copolymerized with EDOT. The stability of these polymers was examined using cyclic voltammetry (CV). The CV curves of the thin films of PEDOTM-C_6-$V^{2+}2PF_6^-$ and the copolymer obtained in the solution of the pure electrolyte have proved the existence of the characteristic, reversible redox system at –0.50 V that is assigned to the viologen radical cation.

Key words: conductive polymers, viologens, PEDOT, spectroelectrochemistry

Among electrically conductive polymers, which often are named synthetic metals, poly(3,4-ethylenedioxythiophene) (PEDOT) is known for its exceptional electrical properties.



This polymer displays relatively low oxidation potential, making possible its easy doping that in turn, directly leads to the conductive form. Besides, PEDOT's monomer may be easy polymerized, both chemically or electrochemically. In the last case, a well adhering film is formed on the electrode surface that is electrochemically active [1]. A high stability of the oxidized, conductive form of the polymer at elevated temperatures and in electrolyte solutions contributes to its potential applications. An important parameter characterizing PEDOT is relatively low band gap, which is equal to 1.6 eV. UV-Vis spectrum indicates strong absorption maximum at wavelength of 610 nm that causes intensive dark blue colour of the solutions of the reduced polymer [2]. When in oxidized state, PEDOT absorbs in near IR range, however due to low absorbance coefficient, solutions are practically colourless [3].

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.
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Thin films of PEDOT that are produced by electropolymerization on the electrode surface have electric conductivity at the level of $10^0 \div 10^2$ S/cm [1]. Together with the high optical transparency, these properties make possible using of the polymer as the electrode material for light emitting diodes and anti-static material in photography [1]. It is used also in fully organic capacitors with solid electrolyte [4–5]. Finally, the good electrochromic properties are used in the new type of glass windows, which may tune a colour and a level of transparency depending on the applied voltage.

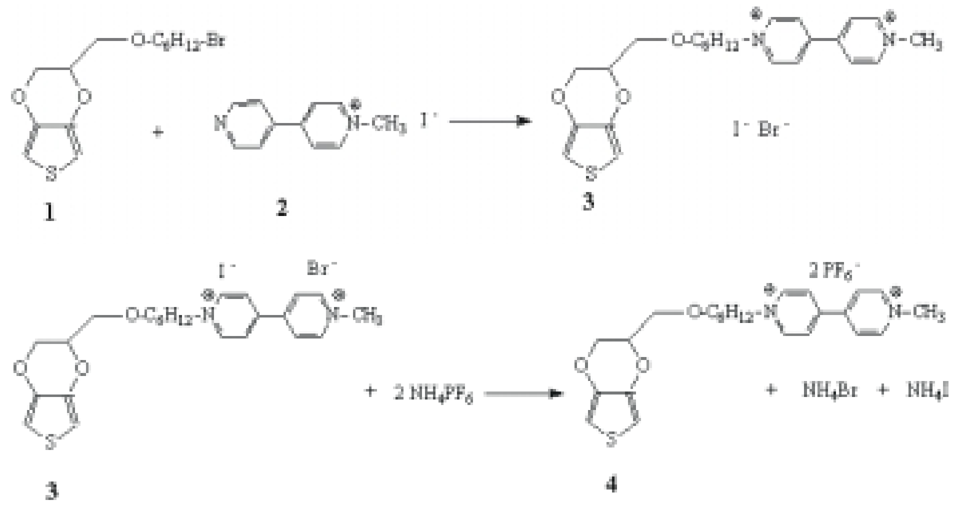
Viologens, a group of 1,1′-disubstituted –4,4′-bipyridinium dications, constitute versatile redox systems with three oxidation states that are colourless as dication, violet as radical cation and yellow to brown in the neutral, fully reduced form [6].

In this paper we describe an attempt to create electrically conductive polymer combining in the same material the valuable features of PEDOT with interesting, well-known redox and electrochromic properties of viologen. Similar idea was recently described for poly(pyrrole-viologen) [7], polythiophene-viologen [8] and poly(cyclopentadithiophene)-viologen [9].

EXPERIMENTAL

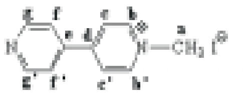
Synthesis of the monomer: 1-methyl-1′(6-(2,3-dihydrothieno[3,4-b][1,4]-dioxine-2-yl-methoxy)-hexyl)-4,4′-bipyridylium bis(hexafluorophosphate), EDOTM-C$_6$-V^{2+}2PF$_6^-$ **4** was obtained in the substitution reaction of EDOTM(CH$_2$)$_6$ bromide **1** (0.0005 M) with N-methyl-4,4′bipyridyl iodide **2** (0.002 M) in acetonitrile. The reaction was carried out under reflux in nitrogen atmosphere during continuous stirring for 48 h. The product obtained, 1-methyl-1′(6-(2,3-dihydrothieno[3,4-b][1,4]-dioxine-2-yl-methoxy)-hexyl)-4,4′-bipyridylium iodide **3** (MVHI) was doubly recrystallized from ethanol and then exposed to PF$_6^-$ in order to exchange the iodide and bromide ions. The final compound was obtained when 0.002 moles of aqueous solution of NH$_4$PF$_6$ was dropped into 0.0005 moles of MVHI in distilled water. The reaction scheme is shown below.

Scheme 1



The structures of the compounds **2** and **4** were confirmed using NMR, MS, and IR spectroscopy. Results are presented in Table 1.

Table 1. Characterization of the synthesized molecules.

	 2	 4
^{1}**H NMR** (ppm)	**(D_2O-TSP)** 4.47 (*s*, 3H; $^+N\text{-}CH_3^a$); 7.92–7.94 (*d*, 2H, CH^c, $CH^{c'}$); 8.396–8.417 (*d*, 2H, CH^f, $C'H^f$); 8.77–8.79 (*d*, 2H, CH^g, $CH^{g'}$); 8.92–8.94 (*d*, 2H, CH^b, $CH^{b'}$)	**(DMSO-TSP)** 1.20–1.40 (*m*, 4H, CH_2^h, CH_2^i); 1.42–1.60 (*m*, 2H, CH_2^j); 1.82–2.10 (*m*, 2H, CH_2^g); 3.49 (*t*, 2H, $^+N\text{-}CH_2^k$, J = 6.7); 3.60–3.70 (*m*, 2H, CH_2^e-O); 3.90–4.00 (*m*, 1H, CH^d); 4.20–4.40 (*m*, 2H, CH_2^c-O); 4.41–4.45 (*s*, 3H, $^+N\text{-}CH_3^s$); 4.68 (*t*, 2H, CH_2^f-O, J = 8.3), 6.57 (*s*, 2H, CH^a-S, $CH^{a'}$-S); 8.77 (*m* 4H, CH^m, $CH^{m'}$, CH^P, $CH^{P'}$); 9.20–9.36 (*d*, 2H, CH^r-N^+, $CH^{r'}$-N^+, J = 6.7), 9.38–9.42 (*d*, 2H, CH^l–N^+, $CH^{l'}$-N^+ J = 6.7).
^{13}**C NMR** (ppm)		**(DMSO-TSP)** 24.9 (**C**H_2^i); 25.1 (**C**H_2^j), 28.7 (**C**H_2^h), 30.6 (**C**H_2^g); 48.0 (**C**H_3-N^{+s}); 60.8 (**C**H_2-N^{+k}), 65.4 (**C**H_2-O^f); 68.4 (**C**H_2-O^e); 70.6 (**C**H-O^d); 72.3 (**C**H_2-O^c); 99.7 (**C**H-S^a); 99.5 (**C**H-$S^{a'}$); 126.0 (**C**H^m, **C**$H^{m'}$); 126.4 (**C**H^p, **C**$H^{p'}$); 141.2 (**C**H^b, **C**$H^{b'}$); 145.7 (**C**H^l, **C**$H^{l'}$); 146.5 (**C**H^r, **C**'H^r); 148.1 (**C**^{n}); 148.4 (**C**^{o})
MS		**[m/e (%)]:[M + Na]$^+$** 738 (5%); $[M\text{-}PF_6^-]^+$; 571.4 (100%)
IR (cm^{-1})		3138 (ν_{CH}); 3074 (ν_{CH}); 2938 (ν_{asCH2}); 2866 (ν_{sCH2}); 1643 (ν_{CaromH}); 1487 ($\nu_{C=C}$); 1193 ($\nu_{C\text{-}O\text{-}C}$); 1019 ($\nu_{C=C}$); 837 ($\nu_{CaromH}$); 780 ($\gamma_{CH}$)

Electrochemical polymerization of the monomer was carried out using cyclic voltammetry (CV) within the potential range of 0.0 V to 1.3 V on the platinum electrode (Pt wire of 0.64 cm^2). Glassy carbon rod, separated from the working electrode space using glass frit, was used as a counter electrode. All potentials are referred to the pseudoreference electrode made of Ag wire. Solutions of monomer containing 0.1 M $TBNPF_6$ as supporting electrolyte were prepared using nonaqueous solvents of high purity, like acetonitrile (ACN) or methylene chloride (MeCl) (Aldrich). In some cases, a mixture of these solvents (3:1) was applied that appears to increase the adherence of the film to the electrode. The charge under voltammetric curves recorded in pure electrolyte was determined to have a comparable thickness of the produced films.

A standard, 1-cm quartz cuvette was used for spectroelectrochemical measurements, in which the same reference and counter electrodes were mounted as in electrochemical cell. A MYLAR, gold-coated optically transparent electrode was applied as a working electrode on which polymer layer was electro-polymerized in a separate cell prior to these measurements. Spectra for solution species were taken on ITO electrode that together with the cuvette wall and Teflon spacer formed a thin layer cell of 80 μm thick. Each spectrum was recorded after equilibrium of the system was reached at the applied potential.

RESULTS AND DISCUSSION

Cyclic voltammetry curves recorded during electropolymerization of EDOTM-C_6-$V^{2+}2PF_6^-$ within potential range of 0÷1.3 V in ACN/MeCl (3:1) mixture at scan rate of 0.1 V/s shown in Figure 1A indicate that the monomer starts to be oxidized at the potential of 1.2 V (for clarity only essential part of voltammogram is presented). This potential is close to the values, which are being found for EDOT and its alkoxylic derivatives [1]. However, in the present case the course of polymerization is different. As shown in Figure 1A, a region of moderately increasing currents is recorded in the potential range 0 to 0.3 V; also an ill-defined redox system occurs at 0.15 V.

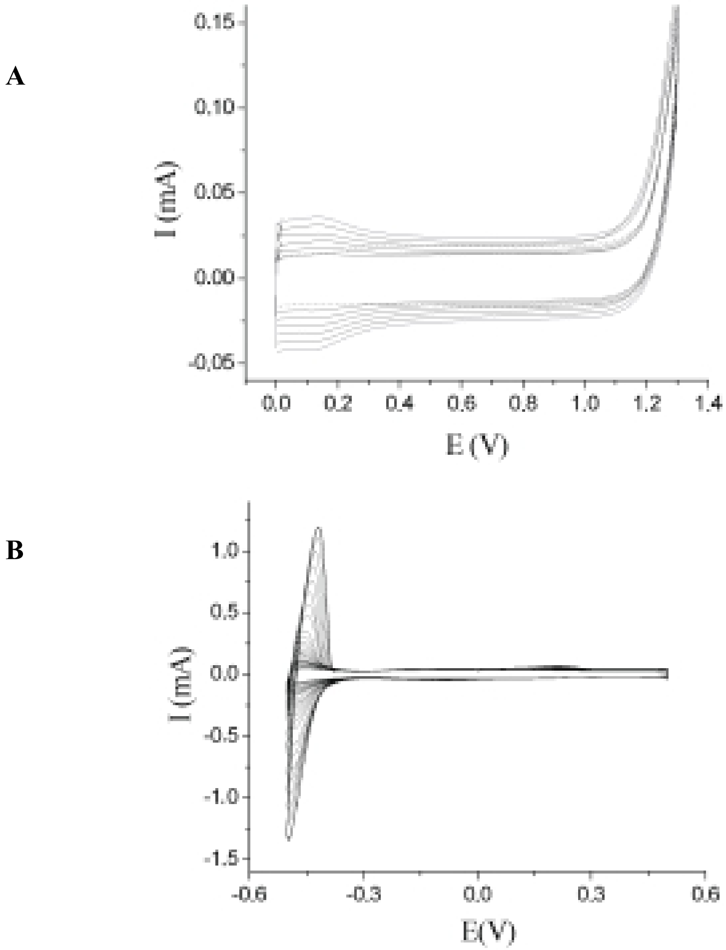


Figure 1. CV curves recorded at scan rate of 0.1 V/s in 0.1 M Bu_4NPF_6 MeCl/ACN (3:1) solution; A) during electropolymerization of 5 mM EDOTM-C6-$V^{2+}2PF_6^-$ (15 scans); B) for PEDOTM-C_6-$V^{2+}2PF_6^-$ film on Pt electrode, the potential range –0.50÷0.50 V.

A progress of the polymerization causes gradually increasing both, anodic and cathodic peak currents. At the same time, one can observe a formation of the dark blue film coating the electrode. The most stable films were obtained at 15 potential cycles. CV curves recorded then in the pure electrolyte, as it is shown in Figure 1B, demonstrate a presence of well-defined redox system at *ca.* –0.50 V that is characteristic for formation of viologen radical cation according to the reaction:

$$\text{PEDOTM-C}_6\text{-V}^{2+}2\text{PF}_6^- \underset{-\,e}{\overset{+\,e}{\rightleftarrows}} \text{PEDOTM-C}_6\text{-V}^{+\cdot}\,\text{PF}_6^-$$

Oxidation of that form takes place at –0.40 V. The product of the oxidation is double charged bipirydynium salt. The highest peak current is observed in the first scan; the following scans reveal a decrease of both, anodic and cathodic peak. If the final potential was extended to the region of the second reduction of viologen (not shown here) then that decrease was much more rapid. Starting from the second CV scan, a new redox system is recorded at 0.17 V /–0.09 V, however its magnitude is gradually decreasing, as may be seen in Figure 2A.

The last effect was assigned initially to an excessive value of the oxidative potential that was applied. However, even if the potential range was shifted to –0.70 ÷ 0 V, a similar results were obtained for the other redox system as it is shown in Figure 2B. Thus, the observed effect cannot be simply a degradation of the polymer; it is a part of a general phenomenon taking place for the system studied. It is likely that electron donating the EDOT-ring interacts with electron accepting the viologen substituent making the electropolymerization more difficult. Additionally some steric effects of bulky viologen moieties may be also involved in the observed phenomenon. However it seems to be less likely, since also in case of other polymers with the pendant viologen groups that effect was not observed [7,8]. Also, the effect of the reduced viologen activity could be responsible for a low efficient doping process, a lowering of the film conductivity, and continuous diminishing of the electroactivity of PEDOT. Therefore, both components PEDOT and viologen are involved in formation of charge–transfer complex within the polymer structure. This conclusion is consistent with another observation, which can be made when these films were produced at different thicknesses. At thinner films the effects related to the diminishing of the redox activity were much less pronounced than that for thick polymer layers.

EDOTM-C$_6$-V^{2+}2PF$_6^-$ was also used as monomer in copolymerization process, together with EDOT at different molar ratio, like: 1:1, 5:1, and 10:1. The CV curves recorded under these conditions, shown in Figure 3A, are generally similar to those described for PEDOT with alkoxy substituents. Although polymerization progresses slowly, increasing redox currents are observed in a wide range of potentials, 0 to 1 V due to formation of the polymer. When the polymer-coated electrode is transferred to the electrolyte solution, the CV curves shown in Figure 3B have been recorded. The clear reduction peak of viologen appears at –0.36 V, which is also decreasing with the number of scans. This result proofs of the existence of viologen units in the copolymer structure.

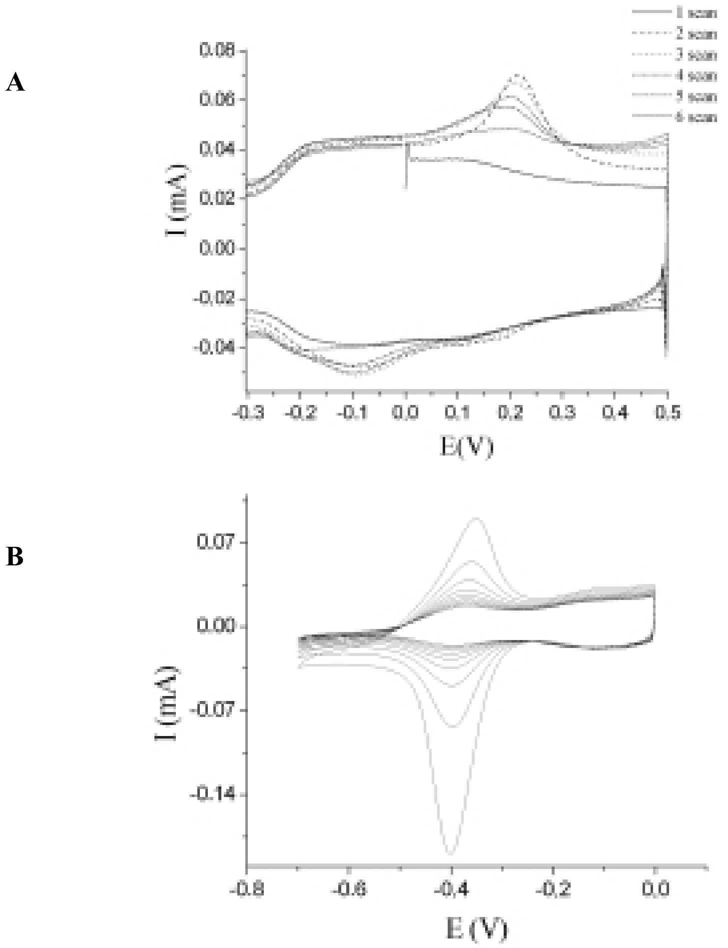


Figure 2. CV curves of the PEDOTM-C_6-$V^{2+}2PF_6^-$ polymer/Pt electrode in 0.1 M Bu_4NPF_6 MeCl/ACN (3:1) at scan rate 0.1 V/s: A) first 6 scans in the potential range: –0.30÷0.50 V; B) in the potential range: –0.70÷0.0 V.

Spectra of the monomer EDOTM-C_6-$V^{2+}2PF_6^-$ in solution, which were taken at the potentials –0.1V to –1.2 V, are shown in Figure 4A. Similar results were recently reported for a polythiophene/viologen [8] and a poly(cyclopentadithiophene)/viologen system [9]. Reduction of the species between 0 V and –0.5 V causes increase of absorbance of the band at wavelengths between 450 nm and 800 nm. That band consists of at least four maxima, at 570 nm, 605 nm, 570 nm, and 735 nm. Besides, a similar trend occurs at the region of higher energies, where absorption peaks at 370 nm, 385 nm, and 396 nm are formed. The spectra recorded at potentials –0.5 V to –0.6 V are practically unchanged indicating an accomplished first reduction step of the viologen component to its radical cation. At the potential of –1.2 V a characteristic spectrum of 4,4′bipiridyl (V^0) is recorded with two maxima, at 370nm and at 396 nm.

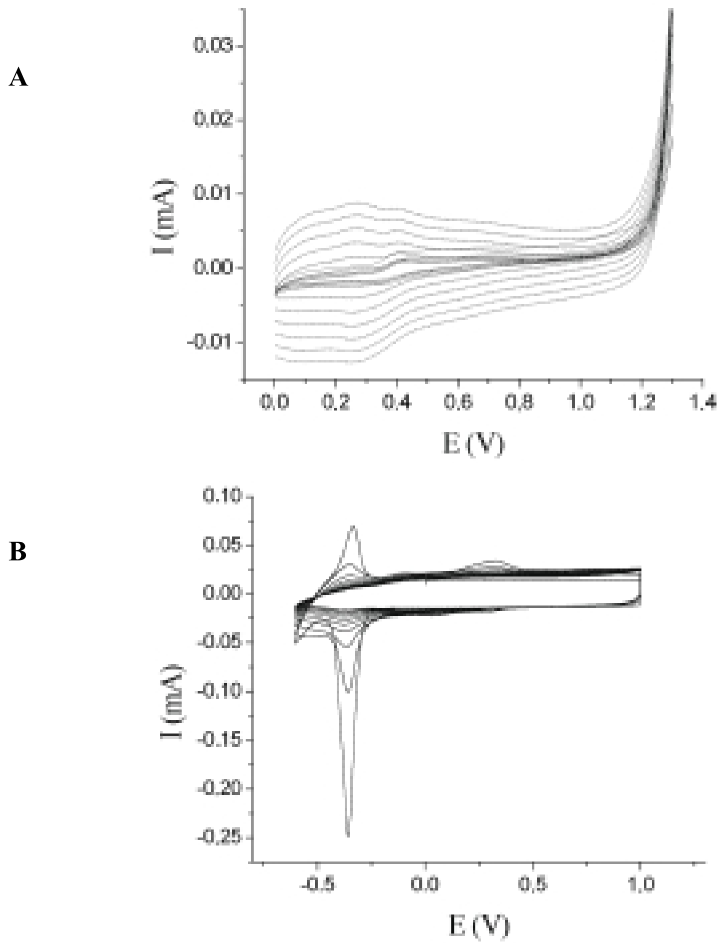


Figure 3. CV curves recorded in solution of 0.1 M Bu_4NPF_6 in MeCl/ACN (3:1) at 0.1 V/s: A) during copolymerization of 5 mM EDOTM-C6-$V^{2+}2PF_6^-$ and 1 mM EDOT; potential range 0 ÷ 1.30 V; first 10 following scans; B) for P(EDOTM-C_6-$V^{2+}2PF_6^-$-*co*-EDOT) (5:1) film in the potential range –0.60 ÷ 1.00 V.

Spectra of polymer film, PEDOTM-C_6-$V^{2+}2PF_6^-$, in the wide range of potentials 1.0 V to –1.2 V are shown in Figure 4B. At positive potentials, between 0 V and 1.0 V a wide band with maximum at 950 nm exists, which gradually decreases and shifts its maximum towards lower energies. Another broad band with maximum at *ca*. 600 nm totally disappears during oxidation of the polymer. At negative potentials, a peak at 400 nm is formed which achieves that maximum at –1.2 V. These trends confirm generally existence of both components in the polymer. However, if the spectra of reduced form of viologen are compared for monomer EDOTM-C_6-$V^{2+}2PF_6^-$ and for the polymer PEDOTM-C_6-$V^{2+}2PF_6^-$, then significant differences are clearly seen as shown in Figure 4C. That bathochromic shift of the absorption maximum from

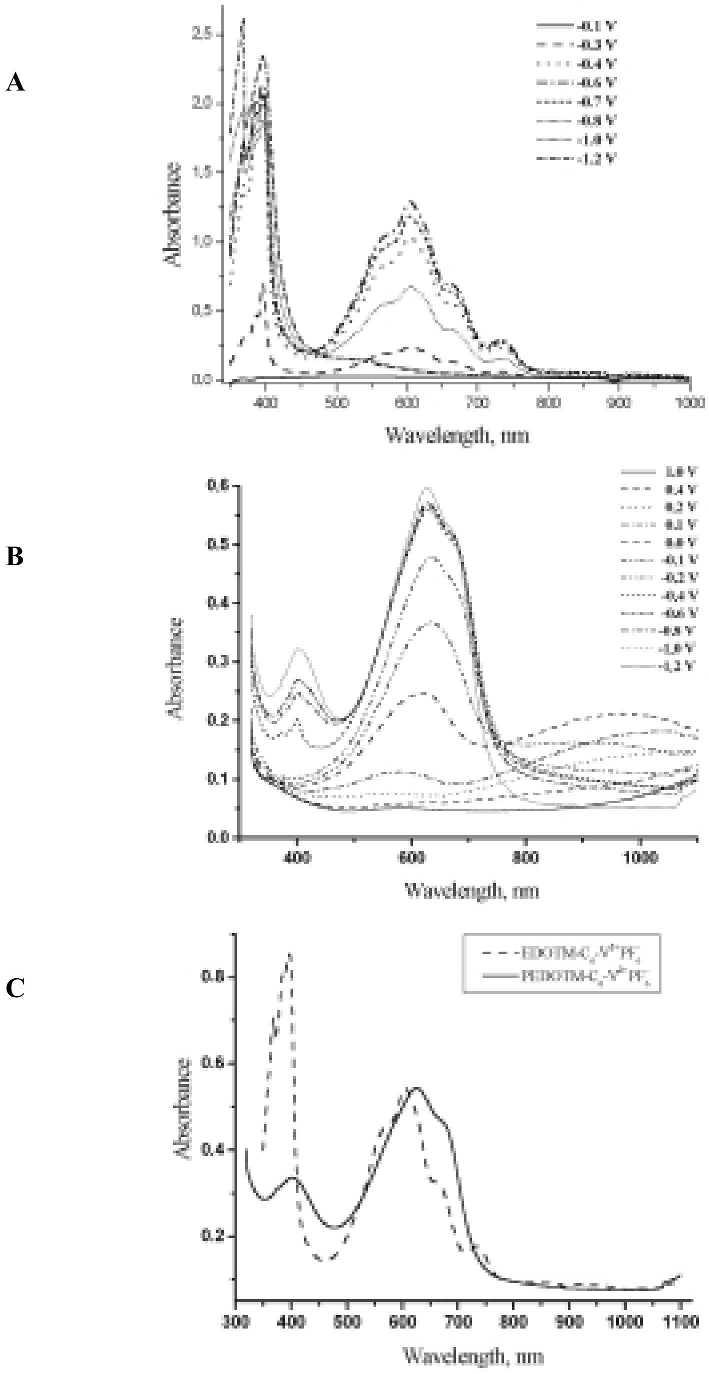


Figure 4. UV-Vis spectra in solution of 0.1 M Bu_4NPF_6 in MeCl /ACN (3:1): A) EDOTM-C_6-$V^{2+}2PF_6^-$ (solution) in the region of negative potentials –0.10 – to –1.20V; B) PEDOTM-C_6-$V^{2+}2PF_6^-$ film; potential range is 1.00 V to –1.20V; C) EDOTM-C_6-$V^{2+}2PF_6^-$ monomer in solution and PEDOTM-C_6-$V^{2+}2PF_6^-$ polymer recorded at the potential E = –0.60 V.

393 nm in monomer to 403 nm in polymer that corresponds to 0.080 eV supports the thesis postulated above on a basis of electrochemical results that the strong interactions between the viologen substituents and EDOT, which take place in the system cause a lowering of its energy.

CONCLUSIONS

- The new synthesized compound, EDOTM-C_6-$V^{2+}2PF_6^-$ used as monomer is able to polymerize under electrochemical conditions.
- EDOTM-C_6-$V^{2+}2PF_6^-$ may form copolymers at various ratios in respect to EDOT, providing electroactive films on the electrode surface. Cyclic voltammetry reveals a presence of viologen substituent both, in polymer and in copolymer.
- Strong interactions between the PEDOT chain and the viologen substituent take place evidently in the new polymer. As a result, a formation of a new redox system is observed in CV curves, simultaneously with decreasing peak current that is responsible for reduction of viologen to radical cation.

Acknowledgment

This paper was supported by Chemistry Department grant BK-207/RCh4/04.

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