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Electrochemical synthesis of polymers with alternate phenothiazine and bithiophene units

Mieczysław Łapkowski[a,b,*], Sylwia Plewa[a], Agnieszka Stolarczyk[a], Jacek Doskocz[c], Jadwiga Sołoducho[c], Joanna Cabaj[c], Mariola Bartoszek[d], Wiesław W. Sułkowski[d]

[a] *Silesian University of Technology, Faculty of Chemistry, Strzody 9, 44-100 Gliwice, Poland*
[b] *PAS, Centre of Polymer and Carbon Materials, ul. M. Curie-Skolodowska 34, 41-819 Zabrze, Poland*
[c] *Wrocław University of Technology, Department of Chemistry, Faculty of Medicinal Chemistry and Microbiology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*
[d] *Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland*

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Abstract

An electrochemical and spectroelectrochemical study of a new monomer—*N*-alkyl-bis(thiophene)phenotiazine have been presented. Electrochemical polymerization of the monomer leads to a polymer with alternate phenothiazine and bithiophene units. Polymerization proceeds after bielectronic oxidation of the molecule. Monoelectronic oxidation gives a stable radical cation with spin located on phenothiazine. Electrochemical properties of the polymer depend on the thickness of the film deposited on the electrode. For thin layers one can observe a characteristic redox couple of phenothiazine oxidation to a radical cation. Analysis of the polymer behaviour and the results of spectroelectrochemical measurements indicate a mixed-type of polymer conductivity.

Keywords: Phenothiazine derivatives; Cyclic voltammetry; Radical cation; ESR; Oxidation mechanism

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1. Introduction

After the discovery of electroluminescence in poly(*para*-phenylvinylene), conducting polymers have been investigated in view of potential applications in electronics and optoelectronics. Special effort has been focused on obtaining light-emitting diodes with active elements composed of organic polymers or conjugated oligomers [1–13]. New materials have been synthesized to improve electroluminescent properties, stability and obtain a suitable colour of light [14–19]. Properties of polymers can be modified by introducing new substituents to the chain or by synthesis of suitable copolymers from two or more monomers, which yield materials with desired properties [20–23].

Chemical polymerization is often used, so solubility of the obtained polymer in organic solvents is important. An alternative method—electrochemical polymerization generally gives materials unsuitable for construction of light-emitting diodes. In recent years some reports showing the applications of electrochemically synthesized materials in electroluminescent devices have appeared [24]. On the other hand, optical devices are among the most promising technologies in terms of economical and technical aspects [25,26]. The construction of electrochromic memories can become one of the most important applications of conducting polymers [27]. For this purpose it is necessary to obtain materials with high-optical contrast and rapidly changing the colour. Common conducting polymers fulfil most of these requirements, but research is carried out to find new better materials. Phenothiazine is one well-known electrochromic compound [28,29], which can be polymerized electrochemically. However, the conductivity of polymers of phenothiazine is low and it is difficult to obtain electroactive films of adequate thickness. This molecule was also used for chemical synthesis of alternating

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[*] Corresponding author at: Silesian University of Technology, Faculty of Chemistry, Strzody 9, 44-100 Gliwice, Poland.
E-mail address: mieczyslaw.lapkowski@polsl.pl (M. Łapkowski).

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photoluminescent copolymers with the phenothiazine in the main chain [29–32].

Electrochemical synthesis offers numerous advantages, which include easy control of the thickness of a deposited polymer and the direct synthesis on any conducting surface, which eliminates the necessity of obtaining processable polymers. In this work we describe the electrochemical and spectroelectrochemical study of a new monomer containing a phenothiazine moiety in the main chain, which give conjugated polymer with interesting electrochemical and electrochromic properties.

2. Experimental

2.1. Materials

Electrolyte solution was prepared by dissolving tetrabutylammonium tetrafluoroborate $TBABF_4$ (Janssen Chimica, 99%) in acetonitrile (CH_3CN for DNA synthesis and peptides, water <10 ppm, POCh, Gliwice, Poland) for cyclic voltamperometry and UV–vis measurements and in dichloromethane (Dichloromethane for spectroscopy stab. amylene, water max. 0.01%, POCh, Gliwice, Poland) for ESR measurements. Concentration of the solution was 0.1 M. All measurements were carried out at room temperature.

The concentration of *N*-butyl-bis-3,7-(thiophene)phenotiazine (BTP_C4) was 1 mM for cyclic voltamperometry and UV–vis measurements and 0.25 mM for ESR measurements. The measurements were done in a three-electrode cell, using 2 mL sample solution. CV and UV–vis spectra of electrodeposited films were taken in monomer-free solutions of the same supporting electrolyte as used for polymerization. Film of poly(BTP_C4) for ESR measurements was electropolymerized in 0.1 M $TBABF_4$ solution in CH_3CN and the ESR spectrum was recorded in 0.1 M $TBABF_4$ solution in dichloromethane.

2.2. Instrumental characterization

Electrosynthesis and studies of polymer films were performed on a computer-controlled Ecochemie AUTOLAB potentiostat—galvanostat model PGSTAT20. The results were analyzed using GPES software (General Purpose Electrochemical System). Cyclic voltammetry (CV) was used for electrochemical measurements.

Polymer film was synthesized directly on the Pt working electrode. A platinum spiral was used as an auxiliary electrode and the potential was measured versus Ag/AgCl reference electrode or Ag wire pseudoreference electrode. Solutions were purged with argon for several minutes.

Spectroelectrochemical measurements were carried out using a UV–vis spectrophotometer Cintra 5 connected with OMNI 9, Cypress 2000 potentiostat. Data were analyzed using OriginPro 7.5 software.

ITO-covered glass electrode served as a working electrode, Ag wire was used as a pseudoreference electrode and platinum spiral was employed as an auxiliary electrode.

ESR spectroelectrochemical measurements were carried out using Bruker ESR spectrometer connected with OMNI 9, Cyperss 2000 potentiostat. ER 041 XG Microwave Bridge X-Band was employed. Results were analyzed using OriginPro 7.5 software.

A NanoScope E (Digital Instruments) with standard electrochemical cell and cantilever of 0.06 N/m spring constant was used in EC AFM measurements.

Infrared spectra of the polymer films were acquired using ATR technique on a Bio-Rad FTS 175C spectrophotometer.

3. Results and discussion

In recent years considerable interest has been focused on phenothiazine derivatives, because of their unique electrochemical and spectroscopic properties [30–37]. But this group of compounds undergoes homopolymerization, giving polymers with low-electric conductivity [38–44]. Improving the conductivity is possible by introducing a fragment, which after oxidation gives a polymer with good electrochemical properties. The simple method was substitution of a phenothiazine molecule at positions 3 and 7 with a heterocyclic compound such as pyrrole, thiophene or furan (Scheme 1).

This type of compound was synthesized according to our previous experience using a multi-step procedure [45].

Experimental results and theoretical calculations suggest that α,α′ positions in the five-membered heterocyclic ring are characteristic places for electrochemical polymerization [46]. The polymerization leads to a copolymer with alternate phenothiazine and biheterocyclic groups (e.g. bithiophene) in the chain. In this paper we report electrochemical and spectroelectrochemical studies of the model monomer and polymer with thiophene as heterocyclic substituents.

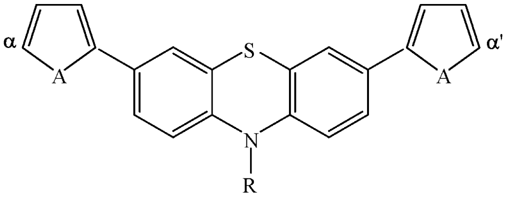
Fig. 1 shows a typical cyclic voltammogram of the monomer BTP_C4. In this case two redox systems are observed in the potential range from −1 to 1.2 V. The first system is reversible at 0.164 V, whereas the second non-reversible at 0.734 V.

According to the literature data [38,39], the first redox system is associated with monoelectronic oxidation of BTP_C4 to a radical cation (Reaction (1)), whereas the second to a dication (Reaction (2)).

$$\mathrm{BTP\_C4} \rightarrow \mathrm{BTP\_C4}^{\bullet +} + e^- \qquad (1)$$

$$\mathrm{BTP\_C4}^{\bullet +} \rightarrow \mathrm{BTP\_C4}^{2+} + e^- \qquad (2)$$

The oxidation potential of the radical cation is close to the oxidation potential of similar phenothiazine molecules, which suggests that additional aromatic rings do not significantly



Where: A – S, O, NH
R – alkyl

Scheme 1.