



The effect of solvent on the synthesis and physicochemical properties of poly(3,4-ethylenedioxyppyrole)



Katarzyna Krukiewicz^{a,*}, Tomasz Jarosz^a, Artur P. Herman^b, Roman Turczyn^a, Sławomir Boncel^b, Jerzy K. Zak^{a,*,1}

^a Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Strzody 9, 44-100 Gliwice, Poland

^b Department of Organic Chemistry, Bioorganic Chemistry and Biotechnology, Silesian University of Technology, Krzywoustego 4, Gliwice 44-100, Poland

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ABSTRACT

Poly(3,4-ethylenedioxyppyrole), PEDOP, is a versatile compound, which has attracted significant scientific interest in the recent years. The wide range of its actual and prospective applications underlines the need for a comprehensive study of this material and identification of factors, allowing the physicochemical properties of PEDOP and its derivatives to be tailored for specific purposes. In this paper, we present the results of our investigation of the physicochemical properties of PEDOP, involving electrochemical, spectroelectrochemical and microscopic analysis. The electrochemical synthesis of PEDOP was performed in solvents of varying polarity and protic/aprotic nature, i.e. H₂O, CH₃CN and CH₂Cl₂, by means of cyclic voltammetry. Raman spectroscopy was applied in order to investigate the chemical structure of PEDOP synthesised under varying conditions. ESR measurements allowed the observation of changes in spin concentration as a function of applied potential and analysis of the stability of formed radical anions. UV–vis spectroelectrochemistry was applied to determine the value of optical band gap of PEDOP. The surface morphology of fabricated PEDOP layers was investigated via scanning electron microscopy.

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1. Introduction

Poly(3,4-alkylenedioxyppyrole)s, PXDOPs, with their low oxidation potentials, multi- electrochromism, high redox switching stability and good resistance to over-oxidation [1], are a promising class of electrically conducting polymers. First synthesised by Merz et al. in 1992 [2,3], PXDOPs became an area of research interest for Reynolds' group, who explored new routes of their synthesis and examined their fundamental properties [1,4–6]. The unique combination of physicochemical properties make PXDOPs ideal candidates for such applications as sensors and biosensors [7–11], dye-sensitised solar cells [12,13], supercapacitors [14], electrochromic displays [15] and, potentially, bioengineering materials [16,17]. The wide range of actual and prospective applications of PXDOPs underlines the need for a comprehensive study of these

materials and identification of factors, allowing the physicochemical properties of PXDOP derivatives to be tailored for specific purposes.

Electrochemical polymerisation is an advantageous method for the synthesis of conducting polymers, because of its reproducibility and wide range of controllable parameters [18]. The electrochemical, physicochemical and mechanical properties of electrodeposited conducting polymers are dependent on numerous variables, most importantly on the nature of the solvent and supporting electrolyte, as well as the conditions of electropolymerisation process [19]. It is possible to obtain polymer films exhibiting different properties, by varying the size and mobility of the counter-anion present in the polymerisation mixture, which is incorporated into the polymer matrix upon p-doping [20]. By altering the electropolymerisation conditions, it is possible to control the growth and uniformity of the polymer layer [21].

Solvent nature, however, is known to influence both the structure and properties of several conducting polymers, particularly polypyrrrole, PPy [20,22] and poly(3,4-ethylenedioxythiophene), PEDOT [23–25], which are both structurally related to PXDOP derivatives. Voltammetric studies of PPy show that the nature of solvent, together with the anion type, influences the

* Corresponding authors.

E-mail addresses: katarzyna.krukiewicz@polsl.pl (K. Krukiewicz), tomasz.jarosz@polsl.pl (T. Jarosz), artur.herman@polsl.pl (A.P. Herman), roman.turczyn@polsl.pl (R. Turczyn), slawomir.boncel@polsl.pl (S. Boncel), jerzy.zak@polsl.pl (J.K. Zak).

¹ ISE member.

redox activity of polymer, its electrochromic properties and the level of doping [20,22]. The reported mechanism, explaining the influence of solvent on electrochromic properties of PEDOT, is based on a conformational change of polymer chains from a coil structure to a linear structure, facilitating charge hopping phenomena in the bulk of the polymer layer, leading to better conductivity and electroactivity [23]. Small angle X-ray studies on PEDOT-PSS in solution confirm that the choice of solvent influences the charge transport in polymeric films [24].

Poly(3,4-ethylenedioxythiophene), PEDOP, is a versatile PXDOP attracting significant scientific interest over the recent years. Structurally related to both PEDOT and PPy, it is expected to exhibit a combination of the qualities of its “parent” polymers, resulting in similar behaviour when electrodeposited in different conditions. In this paper, we present the results of our investigation of the physicochemical properties of PEDOP, involving electrochemical, spectroelectrochemical and microscopic analysis. The electrochemical synthesis of PEDOP was performed in solvents of varying polarity and protic/aprotic nature, i.e. H₂O (polarity index 9.0), CH₃CN (polarity index 5.8), and CH₂Cl₂ (polarity index 3.1) [25], by means of cyclic voltammetry (CV). Raman spectroscopy was applied in order to investigate the chemical structure of PEDOP synthesised under varying conditions. ESR measurements allowed the observation of changes in spin concentration as a function of applied potential and analysis of the stability of formed radical anions. UV–vis spectroelectrochemistry was utilised to determine the value of optical band gap of PEDOP. The surface morphology of fabricated PEDOP layers was investigated via scanning electron microscopy (SEM).

2. Materials and methods

2.1. Materials

3,4-ethylenedioxythiophene, EDOP, was synthesised according to the method described by Merz et al. [3]. Tetrabutylammonium tetrafluoroborate, Bu₄NBF₄ (Aldrich, 99%), ferrocene, Fe(C₅H₅)₂ (Aldrich, 98%) and lithium perchlorate, LiClO₄ (Aldrich, 95%), were used as received. Grade 1 (R > 10 MΩ·cm⁻¹) deionised water, acetonitrile, CH₃CN (CarloErba for HPLC, ACS reagent) and dichloromethane, CH₂Cl₂ (Sigma–Aldrich, Chromasolv™, ≥99.8%), were employed as solvents.

2.2. Electrochemical polymerisation of EDOP

A three electrode, 2 ml electrochemical cell was equipped with platinum wires as the working and auxiliary electrodes. In aqueous solution, Ag/AgCl was chosen as the reference electrode, whereas in non-aqueous solutions Ag wire was employed as a pseudo-reference electrode. The potential of the Ag pseudo-reference electrode was monitored by measuring potential of ferrocene/ferrocenium (Fc/Fc⁺) redox system in 0.1 M Bu₄NBF₄ solution before each electrochemical measurement. All potentials have been calculated versus Fc/Fc⁺ redox system. The electrochemical deposition of PEDOP on the surface of Pt wire was performed by means of cyclic voltammetry (CH Instruments 620 electrochemical workstation) in 0.1 M electrolyte solution containing 10 mM EDOP. In aqueous solution, the polymer film was prepared in 0.1 M LiClO₄, through scanning the applied potential from –0.55 V to 0.75 V (vs. Fc/Fc⁺) at a scan rate of 100 mV s⁻¹. In non-aqueous environment, the polymer film was deposited in 0.1 M Bu₄NBF₄, sweeping the

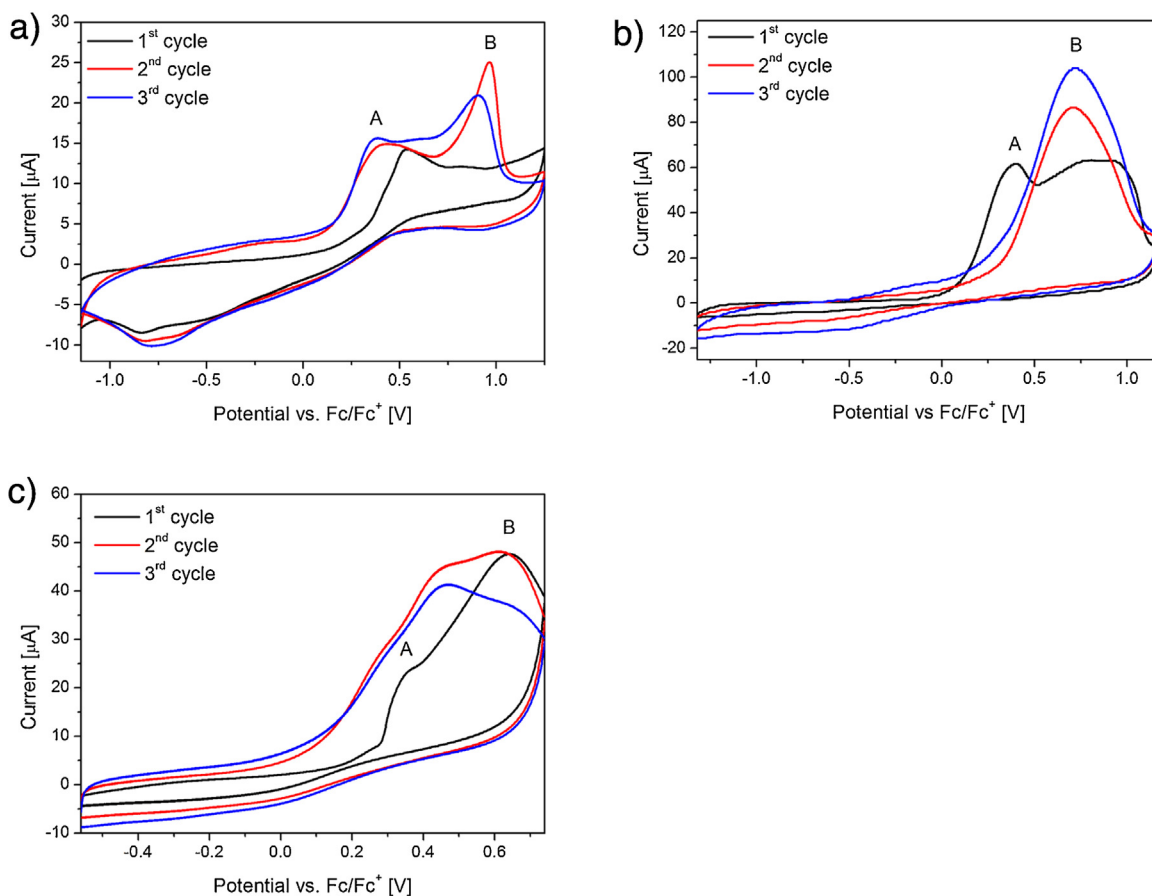


Fig. 1. CV curves recorded during first three potential cycles of the process of electrochemical polymerisation of 10 mM EDOP in CH₃CN (a), CH₂Cl₂ (b) and H₂O (c).

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