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Synthesis and characterization of new copolymer of pyrrole and 3,4-ethylenedioxythiophene synthesized by electrochemical route

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ABSTRACT

A copolymer of pyrrole (Py) and 3,4-ethylenedioxythiophene (EDOT) was electrochemically synthesized on ITO electrode by using potentiodynamic method in acetonitrile with tetrabutylammonium tetrafluoroborate (Bu_4NBF_4). The product poly(pyrrole/3,4-ethylenedioxythiophene) P(Py-*co*-EDOT) was characterized via CV, FTIR and SEM. Copolymer film has distinct properties, i.e., these were homogeneous and exhibited good electrochemical properties.

1. Introduction

Since the discovery of conducting polymers by H. Shirakawa, published in 1977, synthetic metals (more commonly known as conductive polymers) have attracted attention of researchers from all over the world. Synthetic metals are a class of compounds that combine the typical properties of conventional plastics with the properties of electrically conductive materials. Moreover, they have many favorable properties such as environmental and thermal stability, high conductivity and small band gaps. These properties of synthetic metals allow for a wide range of commercial applications [1], as well as prompt both academic and industrial environments to design and synthesize them and to study of their properties.

Copolymerization is one of the common methods of preparing polymeric materials with desirable and strictly defined properties. Usually via electrochemical polymerization copolymers are obtained using complex multifunctional monomers [2]. However, it is important to investigate the process of electropolymerization from the mixture of monomers, which offer easier way for commercial application of the process. This method offers the possibility of obtaining materials with characteristic properties of their individual components, and thus expands the scope of application of a given polymer in various fields. In the last years, the excellent properties of poly(3,4-ethylenedioxythiophene) (PEDOT) [3] have been combined with those of other typical conducting polymers. So far, copolymers of 3,4-ethylenedioxythiophene (EDOT) with thiophene [4,5], naphthalene [6] or pyrene [7] has been successfully obtained and studied. In the literature of recent years are also described interesting properties of polypyrrole (PPy) [8] and polymers of substituted pyrrole (Py) [9–13]. One of the most important method of the synthesis of conducting polymers is electropolymerization. The products of polymerization reactions are deposited on various electrodes, such as metallic electrodes, steel electrodes [3,14], carbon fibers [15], glassy carbon [9] or ITO [6,16–18]. A significant effect on the electrical properties, morphology and the electrode coverage have the electrode material, the solvent [19], and concentration of the electrolyte [20] used in the synthetic route. All these factors are being studied in various laboratories all over the world. Currently, conductive polymers are used, among others, for the production of biosensors, transistors, electrochromic devices, optical displays, light emitting diodes and photovoltaic cell [21].

The goal of present study is to synthesize a new copolymer of pyrrole and 3,4-ethylenedioxythiophene and determine the physicochemical properties of this material. Polypyrrole is a common conducting polymer easily synthesized using electropolymerization and relatively chip. However, it is somewhat unstable in ambient. On the other hand, PEDOT is well known and widely used in commercial applications having strong intramolecular S:O interactions reported as disadvantage of the polymer [22]. On the other hand, the monomer for this material is more sophisticated and expensive. Synthesis of the copolymer from

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equimolar mixture of EDOT and pyrrole gives an opportunity to obtain and investigate intrigue new material with properties resulting from combination of two known, conducting polymers and introduce the material which is not only attractive due to its properties but also chipper.

In this paper, we report the synthesis and investigation of properties of the copolymer of pyrrole and EDOT in comparison to polypyrrole and poly(3,4-ethylenedioxythiophene) homopolymers synthesized in the same conditions. For deeper understand of the new material on the molecular level quantum chemical calculations are included. All compounds studies in this study were characterized using methods such as cyclic voltammetry, FTIR spectroscopy, thermal analysis and scanning electron microscopy.

2. Materials and methods

Pyrrole (98%, Aldrich), 3,4-ethylenedioxythiophene (97%, Aldrich), tetrabutylammonium tetrafluoroborate (99%, Aldrich), acetonitrile (99,5%, POCH) were used as received. Indium tin oxide – ITO coated poly(ethylene terephthalate) – PET (Aldrich) was first cleaned with acetone in ultrasonic bath.

The electrochemical experiments, were performed using Autolab PGSTAT128N potentiostat/galvanostat. The electrochemical experiments were carried out using three electrode system consisting of an indium tin oxide (ITO)—coated poly(ethylene terephthalate) substrate as the working electrode the Ag/AgCl reference electrode and Pt counter electrode. All electrochemical measurements were performed using cyclic voltammetry.

The electrochemical process of the monomer oxidation, as well as about the electrochemical properties of the resulting polymer material. The electrochemical synthesis were carried out in deareated acetonitrile containing 7.5×10^{-3} mol dm^{-3} of the monomer in the experiments were performed to provide information about the presence of electrolyte Bu_4NBF_4 (0.1 mol dm^{-3}), in the copolymerization route equimolar mixture of the two monomers were used (3.75×10^{-3} mol dm^{-3} of pyrrole and 3.75×10^{-3} mol dm^{-3} of 3,4-ethylenedioxythiophene). The investigation of electrochemical properties were conducted in similar electrolyte system without the presence of monomers. The experiments were carried out at temperature 298 ± 0.5 K.

In order to determine the current-voltage characteristics and volume dc-conductivity (σ_{dc}) of polymer samples pressed powder pellets were prepared by pressing ground polymer in the laboratory press under pressure 70 bar. Afterwards the gold contacts were evaporated in vacuum. Afterward measured the thickness of the prepared structures. Measurements were performed applying two point probe electrometer. The pellets were tested at three different temperatures 298, 308, 318 K. The Activation energy of electric conductivity of the materials in the native state was measured in the systems analogous to above. The pellets were placed in a thermostatic chamber (293–473 K) and constant voltage 25 V was applied while the fluctuation of dc-current was recorded. Kinetics of iodine doping was investigated in the measuring vessel consist of the thermostated iodine source and two electrode electrometer terminal. The tests were

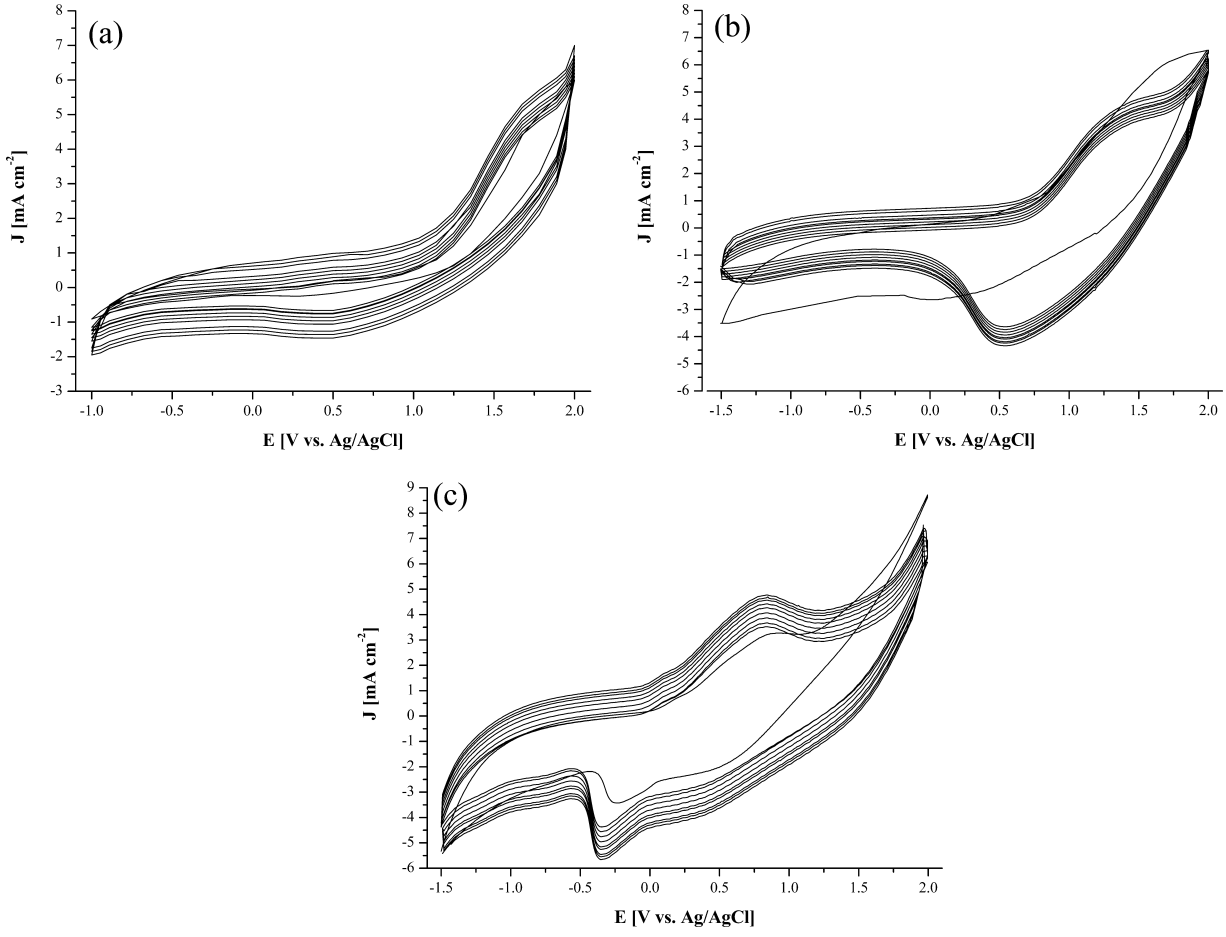

Fig. 1. Cyclic voltammogram of (a) 7.5×10^{-3} mol dm^{-3} of Py (b) 7.5×10^{-3} mol dm^{-3} of EDOT (c) equimolar mixture of Py and EDOT (3.75×10^{-3} mol dm^{-3} of Py and 3.75×10^{-3} mol dm^{-3} of EDOT), scan rate 0.1 V s^{-1}.