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Electrochemical synthesis, characterization and capacitive properties of novel thiophene based conjugated polymer



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ABSTRACT

In this paper, a novel thiophene based monomer, *1-(pyren-1-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole*, PThP, was synthesized and characterized by ¹H NMR and ¹³C NMR spectroscopic methods. The electrochemical behavior and electropolymerization of this novel monomer were performed on pencil graphite electrode (PGE) by cyclic voltammetry. The effect of solvent, dopant, scan number and scan rate on the electropolymerization and properties of the conjugated polymer films were investigated. The capacitive properties of the poly(PThP) films were tested by electrochemical impedance spectroscopy (EIS). The highest specific capacitance value was calculated for the conjugated polymer modified PGE that was obtained in 0.1 M tetrabutylammonium perchlorate/dichloromethane solution for 30 cycles at 25 mV/s scan rate as 25.45 mF cm⁻². The surface morphologies of the conjugated polymer modified electrodes were determined by scanning electron microscopy (SEM).

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1. Introduction

Electrochemical capacitors, often called supercapacitors, electrical double-layer capacitors, pseudocapacitances or ultracapacitors have attracted worldwide research interest because of their potential applications as energy storage devices in many fields [1]. The enormous progress in supercapacitor technology, resulting in electrode materials with higher and higher specific capacitance values, has led to extension of their application [2]. Supercapacitors can store more energy than a conventional capacitor because: (i) charge separation takes place across a very small distance in the electrical double layer that constitutes the inter phase between electrode and electrolyte; and (ii) an increased amount of charge can be stored on the highly extended electrode surface area created by a large number of pores within an electrode material. The mechanism of energy storage is naturally rapid because it simply involves movement of ions to and from electrode surfaces [3].

On the basis of electrode materials used and the charge storage mechanisms, electrochemical supercapacitors are classified as: (a) electrical double-layer capacitors which employ carbon or other similar materials as blocking electrodes and (b) redox supercapacitors in which electroactive materials are used such as insertion type compounds (e.g. RuO₂, NiO, etc.) or conjugated polymers (CPs) [4].

These organic polymers possess conductive chain structures and electrical conductivity [5]. The conjugated polymers of unique properties such as mechanical strength, electrical conductivity, remarkable stability and possibility of both chemical and electrochemical synthesis and low bandgap, have received great attention. Therefore, they are used in potential applications in various emerging fields such as transparent electrodes, OLEDs, rechargeable batteries, electrochromic displays and smart windows, light emitting diodes, sensors, corrosion inhibitors, field effect transistors (FETs), electromagnetic interference (EMI) shielding and electrochemical supercapacitors, etc. [6-9]. CPs are promising materials for the realization of high performance supercapacitors, as they are characterized by high specific capacitances and by high conductivities in the charged states. Furthermore, their charge-discharge processes are generally fast. These features suggest the possibility to develop devices with low equivalent series resistance (ESR) and high specific energy and power [10].

Electrochemical synthesis of conjugated polymers has some advantages. For instance, it permits the synthesis without using oxidizing agent together with doping with different organic and inorganic ions. In addition, it is a simple and relatively inexpensive method. By adjusting the conditions, both powders and films can be obtained and also this allows controlling thickness [11,12]. In

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the electropolymerization process of the conducting polymers, two oxidation reactions occur simultaneously. The oxidation of monomers and oligomers and the oxidation of a polymer form on the electrode surface producing positive charges (polarons and/or bipolarons). The positive charges are compensated by the anions such as chloride, perchlorate, sulfonate, in the electrolyte solution which is called doping process [13]. In this process, it is possible to control the electrical conductivity of polymer over the range from insulating to highly conducting state. In addition simple modifications of the experimental parameters, e.g. changing the electrode material or solvent, result in changes in the electropolymerization process and in the properties of the final film [14].

Pyrrole, aniline, thiophene and their derivatives can be polymerized to get conjugated polymers by electrochemical synthesis [15]. Electrodeposition of conductive polythiophene (PTh) films by electrochemical oxidation of thiophene and its derivatives has been widely described in recent years [16]. Polythiophenes and their derivatives present an important class of conjugated polymers that form some of the most environmentally and thermally stable materials in both doped and undoped states. These polymers have various useful properties like having high-charge carrier mobilities and high thermal and photochemical stability. In addition, they easily form relatively stable radical cations (holes) [17,18]. PTh and its derivatives are one of the most promising supercapacitor materials and has received a significant amount of attention in applications [19].

Carbon in its dispersed and conducting form is the most widely used commercial material for electrochemical supercapacitors applications as an electrode material. Among carbon based materials, PGE can be seen an important electrode material due to its large active electrode surface area, high electrochemical reactivity, good mechanical rigidity, low cost, disposable and wide potential window. It can be also easily modificated and miniaturized. A combination of conjugated polymers and carbon for positive and negative electrodes in supercapacitors is both scientifically and commercially applicable due to the low cost of the two materials [20–22].

EIS is an attractive method to study the electrical behavior of coated and uncoated neutral prosthetic devices. It involves measuring the electrode impedance over a spectrum of frequencies. By using magnitude and phase information data, one can obtain qualitative and quantitative information about the electrical properties of the coated and uncoated electrodes. Interesting information can be obtained concerning potential distribution across the interface, doping level, solution resistance, carrier recombination and generation at the surface and in the space region. To determine the magnitude of the resistive and capacitive response, their performance can be examined in a wide range of frequencies [23,24].

In this work, a novel thiophene derivative, *1-(pyren-1-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole*, PThP, (Scheme 1) was synthesized by a chemical method and electropolymerized on PGE as an electrode material for supercapacitor applications for the first time in this work. The effect of solvent, dopant ions, scan rate and scan number on electropreparation and properties of the poly(PThP) films were investigated. ¹H NMR and ¹³C NMR spectroscopic methods were used to characterize the PThP. The properties of the polymer were studied in detail using cyclic voltammetry. The capacitive properties of the modified poly(PThP)/PGEs were tested by electrochemical impedance spectroscopy. The surface morphology of conjugated poly(PThP) films was investigated by SEM.

2. Experimental

2.1. Materials

Glassware was routinely oven-dried at 110 °C for a minimum of 4 h. Column chromatography was performed on silica-gel 70–230



Scheme 1. The chemical structure of 1-(pyren-1-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole.

mesh. Dichloromethane (HPLC grade, 99.9%) and acetonitrile (HPLC grade, 99.9%) were purchased from Sigma–Aldrich. All chemicals were analytical grade reagents and were used without further purification. Tetrabutylammonium tetrafluoroborate (TBABF4) (>99%), tetrabutylammonium perchlorate (TBAP) (>99%) and tetrabutylammonium hexafluorophosphate (TBAPF6) (>99%) were obtained from Fluka.

2.2. Synthesis of PThP

1,4-di(thiophene-2-yl)butane-1,4-dione was synthesized according to literature procedure [25]. A solution of 500 mg (2 mmol) 1,4-di(thiophen-2-yl)butane-1,4-dione, 434 mg (2 mmol) 1-aminopyrene and catalytic amount of p-toluenesulfonic acid (p-TsOH) in dry toluene were refluxed in a Dean–Stark apparatus until all the starting materials were disappeared on TLC. The flask was cooled and the solvent was removed under reduced pressure. The residue was placed in a silica-gel column with dichloromethane (CH₂C₁₂) to give the pure PThP monomer. Synthesis route of the PThP is shown in Scheme 2.

NMR spectra were recorded on a Bruker Advance 500 DPX spectrometer (¹H at 500 MHz and ¹³C at 125 MHz) in chloroform-d (CDCl₃) with tetramethylsilane (TMS) as the internal standard.

2.2.1. 1-(pyrene-6-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole

Yield 64%; Orange solid; *M*p = 244–246 C. ¹H NMR (500 MHz, CDCl₃): δ 6.39 (s, 2H), 6.58 (s, 2H), 6.80 (br, s, 4H), 7,61 (d, *J* = 8.5, 1H), 8.06 (m, 3H), 8.21 (m, 3H), 8.28 (t, *J* = 9.5, 2H), ¹³C NMR (125 MHz, CDCl₃): δ 109.75, 122.10, 123.64, 123.68, 124.40, 124.90, 125.05, 125.92, 126.52, 126.73, 127.28, 128.06, 128.59, 129.34, 130.75, 130.96, 131.10, 131.48, 132.07, 132.11.



Scheme 2. The synthesis route of the PThP.

2.3. Electropolymerization and cyclic voltammetry

Electropolymerization of PThP was performed on the surface of PGE by cyclic voltammetry at ambient conditions. Three electrode system was used for all measurements; pencil graphite and platinum electrodes as the working electrodes and a Pt auxiliary electrode. All measurements were carried out with an Ag/AgCl reference electrode.

A Noki pencil model 2000 (Japan) was used as a holder for graphite leads (Tombo, HB, 0.5 mm diameter, Japan). Electrical contact with the lead was obtained by soldering a metallic wire to the metallic part. PGEs were washed with water and dichloromethane to remove the impurity and dried at room temperature before the experiments. Then, PGE was immersed in the polymerization solution. The poly(PThP) was obtained by electrodeposition on the surface of the working electrodes in dichloromethane and acetonitrile solutions of 0.1 M TBABF4, TBAP and TBAPF6 with 0.01 M PThP. Electrochemical studies were performed with a Autolab PGSTAT 100 potentiostat–galvanostat controlled by a GPES 4.9 software (Ecochemie, The Netherlands).

2.4. Electrochemical impedance spectroscopy (EIS)

EIS measurements were performed at room temperature using a conventional three electrode cell configuration. In all impedance measurements, PGE was used as working electrode, platinum wire was used as counter electrode, and Ag wire was used as reference electrode. The electrochemical cell was connected to a potentiostat (PARSTAT 2263) interfaced to a computer. The electrochemical impedance software PowerSine was used to carry out impedance measurements scanning in the frequency range between 10 MHz and 100 kHz with an applied AC signal amplitude of 10 mV.

2.5. Morphological analysis

The morphological features of the electrocoated electrodes were performed with scanning electron microscope (SEM). The pencil graphite electrodes were attached on a metal holder by use of a double sided carbon type. SEM measurements were carried out via Zeiss-Ultraplus.

3. Results and discussion

3.1. Electropolymerization and characterization

To determine the effect of monomer concentration on the yield of electropolymerization, the poly(PThP) films were grown in solutions of varying PThP concentrations in the range of $10-4 \text{ M}-5 \times 10^{-2} \text{ M}$ on a Pt plate electrode by the cycling of the potential between -0.3 and 1.9 V (vs. Ag/AgCl) for the same cycles. 0.1 M TBAP was used as the supporting electrolyte in the electropolymerization. Solubility of PThP decreased with increasing amount of PThP in acetonitrile solutions. Therefore, dichloromethane was used as a solvent in the electropolymerization of PThP. The optimum PThP concentration was found to be 0.01 M (Fig. 1). There was a considerable decrease in the yield of polymer formation below and above this PThP concentration under these conditions was about 0.01 M.

Fig. 2 shows the initial five cyclic voltammetric sweeps taken during the oxidation of 0.01 M PThP in 0.1 M TBAP/dichloromethane solution. The potential was scanned from -0.30 to +1.90 V (vs. Ag/AgCl) at a scan rate of 75 mV/s. The oxidation peak of the PThP shifts to higher anodic potentials. It shows the formation of a film on the electrode surface and behaves different from that of



Fig. 1. The effect of PThP concentration on the yield of electropolymerizations.



Fig. 2. The five initial cyclic voltammograms of 0.01 M PThP in a dichloromethane solution containing 0.1 M TBAP. The scan rate was 75 mV/s.

bare PG working electrode. The formation and growth of the polymer film can easily be seen in this figure suggested that the films were conductive and electroactive [16]. The oxidation and reduction peaks of the film increase in intensity as the film grows. There are one broad oxidation and reduction peaks observed during the growth of the film. The oxidation peak was observed at the peak potential of +1.04 V with corresponding cathodic peak at +0.60 V belonging to the reverse process.

The effect of electrode type on the electropolymerization of PThP (0.01 M) was investigated. The films were grown on a Pt plate and a PGE in a dichloromethane electrolyte solution containing of 0.1 M TBAP by cycling of the potential between -0.30 to +1.90 V (vs. Ag/AgCl) at a scan rate of 100 mV/s. Fig. 3 shows the results of such a comparison. The reduction peak obtained during the growth of the polymer on the surface of PGE shifted to more cathodic potentials according to Pt electrode as the scan number increases. This result may indicate that higher polymer chains are formed on the surface of PGE [26]. Due to the nature of two different electrodes, the bonding of polymer onto PGE would be easier than on Pt. This may also influence the kinetics of polymerization leading to a shift in peak potential, with a greater shift for the PGE electrode than the Pt electrode being expected.

The modified electrodes prepared electrochemically were immersed in dichloromethane to remove monomer and the soluble oligomers formed during electropreparation of the film and then vacuum dried. The electrochemical behavior of the modified electrodes in monomer free electrolyte solutions containing different types of dopants at different scan rates are shown in Fig. 4. The modified film electrodes did not lose their electroactivity and exhibit broad oxidation and reduction peaks in monomer free electrolyte solutions.



Fig. 3. Cathodic peak potential shifts vs. scan number for solutions of monomer on pencil graphite and Pt electrodes in 0.1 M TBAP/dichloromethane solution at 100 mV/s scan rate.

3.2. Effect of dopant ions

To determine the effect of different dopant ions on the growth of the polymer film, the films were grown in dichloromethane solutions containing 0.1 M TBABF4, TBAP and TBAPF6 by cycling the potential between -0.30 and +1.90 V with different scan numbers. Fig. 5 shows the change in anodic and cathodic peak currents of monomers during the electropolymerization in these electrolytes solutions at the scan rate of 100 mV/s. The anodic and cathodic peak currents were measured during the electro-oxidation of the monomer. The different slopes, dl/dt, were obtained in different supporting electrolytes corresponding to the growth rate of polymer film on the PGE surface. As shown in Fig 5, the growth of the polymer film was not regular in TBAP/dichloromethane solution. The anodic and cathodic peak currents ratios of slopes were

5:4 and 3:2 for TBAPF6:TBABF4, respectively. These results indicate that the electrochemical polymer growth rate ratio was faster in TBAPF6 than the others.

3.3. Surface morphology

Dielectric, electrical, and mechanical properties, the film formation and surface morphology of conducting polymers are affected by various parameters: such as nature of solvent and dopant anion, solution pH, temperature, synthesis method, scan rate. Poor control of these parameters will result in dendritic morphology. Dendritic surface will cause interfacial problems in electronic device applications, such as Schottky junctions, and also introduce large errors into the direct current (DC) conductivity measurements by the four probe method due to the errors in polymer thickness determination [27–29]. Therefore, polymer films were deposited from 0.01 M solution of the PThP on to PGE by cyclic voltammetry at different scan rates, dopants and scan numbers to investigate their effect on the morphology of the polymer film. Their morphologies were monitored using SEM. As shown in Fig. 6(a) and (b) and (e) and (f) the thickness of the polymer film is a function of cycle number and scan rate. The film thickness increases linearly with increasing of the number of cycle numbers and decrease linearly with increasing of the scan rate. In Fig. 6(b), it is clearly showed that the surface of the graphite electrode was not completely covered with the polymer. When Fig. 6(e) is compared with Fig. 6(f), small grains are formed on the electrode surface in low cycle numbers. This also explains why we could not obtain high capacitances values for the polymers deposited at low number of cycle. The effects of different dopant anions on the morphology of the film are shown in Fig. 6(c) and (d).

3.4. Electrochemical impedance spectroscopy measurements

EIS was performed to monitor electrochemical behavior of the composite electrodes. EIS is believed to be a good technique for decoupling the electrochemical and mass-transport processes in



Fig. 4. The electrochemical behavior of the poly(PThPs) in monomer free dichloromethane solutions of (a) 0.1 M TBAPF6, (b) TBABF4 and (c) TBAP at different scan rates: 25, 50, 100, 200, 400 mV/s.



Fig. 5. The anodic and cathodic peak currents of poly(PThPs) during polymer growth.

the redox mechanisms of polymers and studying capacitance value of modified electrodes [30,31].

For DC measurements, Ohm's law, V = IR, is used the describe relationship between voltage, current and resistance. For AC measurements, Ohm's law is changed to V = IZ, where the impedance Z, is used rather than resistance in order to allow for frequency dependence and phase shifts between stimulus and observed response. Such properties do not occur in resistors, which have an impedance equation of Z = R [32]. Instead of resistance, impedance is used in electrochemical system because it is a more general circuit parameter. Like resistance, impedance is a measure of the ability of an equivalent circuit to resist the flow of electrical current. Different from resistance, impedance is not limited by the properties of the ideal resistor The expression Z is composed of a real (Z_{re}) and an imaginary part (Z_{im}) . The standard impedance plot used to characterize a conducting polymer is the Nyquist plot on which the real part is plotted on the X-axis and the imaginary part on the Y-axis of a chart. [33].

The low frequency capacitance values of the polymer film at 0.01 Hz and 100 kHz from impedance spectroscopy were obtained from the slop of a plot of imaginary component (Z_{im}) of the impedance at low frequencies versus inverse of the reciprocal frequency (f: 0.01 Hz) using following equation [34]:

$$C_{\rm sp} = (2\pi f Z_{\rm im})^{-1} \tag{1}$$

The specific capacitance values of the polymers, which are electrodeposited in the different dopant ions, cycle numbers and

Table 1

The capacitance values of the polymer films which synthesized in different scan numbers and scan rates.

Scan rate (mV/s)	Scan number		
	10 (F)	20 (F)	30 (F)
25	1.712×10^{-3}	5.031×10^{-3}	6.044×10^{-3}
50	3.829×10^{-3}	$3.579 imes 10^{-3}$	4.413×10^{-3}
75	2.732×10^{-3}	$5.157 imes 10^{-3}$	$4.309 imes 10^{-3}$
100	$\textbf{3.523}\times \textbf{10}^{-3}$	$\textbf{2.978}\times \textbf{10}^{-3}$	3.195×10^{-3}

scan rates were calculated from the Nyquist diagrams. The highest capacitance values as 6.044 mF were detected for the polymer that was obtained in 0.1 M TBAP/dichloromethane solution for 30 cycles at 25 mV/s scan rate (Table 1). 1.5 cm of the PGE was dipped into the solution to keep the electrode area constant (~0.2375 cm²). According to EIS measurements, modified PGE has shown the specific capacitance of 25.45 mF cm⁻² at 25 mV s⁻¹ scan rate and 30 cycles in 0.1 M TBAP/dichloromethane electrolyte solution.

In the literature, different electrode materials were used for supercapacitor applications. Among these materials, poly[3,4-(2,2-dimethylpropylenedioxythiophene)] was electropolymerized on a bundle of carbon fiber microelectrodes (CFMEs) and reported a low frequency capacitance value of 12.05 mF cm⁻². Using a standard three electrode system in sodium perchlorate (NaClO₄)/ACN at open circuit potential a double layer capacitance value of 14.4 mF cm $^{-2}$ was reported. For exfoliated carbon fibers (ExCFs) capacitances of 117–450 F g⁻¹ at surface areas from 330 to $300 \text{ m}^2 \text{ g}^{-1}$ were mentioned. These values are equivalent to $0.035-0.15 \text{ mF cm}^{-2}$. 3,4-(2,2-dibutylpropylenedioxy)thiophene (ProDOT-Bu₂) was electrodeposited onto single carbon fiber microelectrode (SCFME) and calculated specific capacitance value as 62 mF cm⁻² in ACN electrolyte solution containing NaClO₄ as dopant [35]. These results have shown that poly(PThP)/PGE has much higher specific capacitance than other modified electrodes just expect the modified 3,4-(2,2dibutylpropylenedioxy)thiophene SCFME.

It is well known that if the phase angle is greater or equal to 90°, the modified electrode behaves like an ideal capacitor. On the other hand, if the phase angle is less than 90° then the modified electrode is easily allowing the ions from solution. It can be seen in Fig. 7(b) that the values of phase angles for the polymer film is less than 90° and thus the polymer film is not behaved like an ideal capacitor [30].



Fig. 6. SEM images of the polymer films deposited by cyclic voltammetry with a same monomer concentration (0.01 M); change number of cycles, different scan rates and dopants: (a) 30 cycle, 25 mV/in TBAPF6, (b) 30 cycle, 100 mV/s in TBAPF6, (c) 30 cycle, 25 mV/s in TEABF4, (d) 30 cycle, 25 mV/s in TBAPF6, (e) 30 cycle, 30 cycle



Fig. 7. (a) Nyquist and (b) Bode plots of the polymer film on the graphite electrode in 0.1 M TBAP/dichloromethane solution.

4. Conclusions

A novel thiophene derivative, 1-(pyren-1-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole, PThP, was synthesized by chemical method and electropolymerized on the surface of PGE for the first time in this work. ¹H NMR and ¹³C NMR spectroscopies were used to characterize the PThP. The effect of solvent, dopant ions, scan rate and scan number on the electropreparation and properties of the poly(PThP) films were investigated. The properties of the polymer were studied using cyclic voltammetry and scanning electron microscopy techniques. The SEM pictures show that the electropolymerization of monomer was successfully occured on the surface of PGEs. Cyclic voltammograms indicate that the choice of dopant ions has influenced on the electropolymerization process. In addition, the influences of scan rate, cycle number and dopant ions on the morphology of polymer film are clearly shown in the SEM images. The capacitive properties of the poly(PThP) films were tested by electrochemical impedance spectroscopy. The highest specific capacitance value was obtained for the polymer that was synthesized in TBAP/dichloromethane solution with 25 mV/s scan rate and 30 cycles as 25.45 mF cm⁻². As a result, this modified PGE can be used as an electrode material for supercapacitors in the low voltage applications.

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