UNIVERSITI PUTRA MALAYSIA

ELECTROPOLYMERIZATION AND CHARACTERIZATION OF POLY(3,4-ETHYLENEDIOXYTHIOPHENE, POLYANILINE, POLYPYRROLE AND THIER COPOLYMERS

SHALINI KULANDAIVALU

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By

SHALINI KULANDAIVALU

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in fulfilment of the requirement for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman: Dr Yusran Sulaiman, PhD
Faculty: Science

In recent years, conducting polymers have served as a core material for many new applications such as sensors, solar cells and electrochromic display devices. Among the methods to prepare conducting polymers (CPs), electrochemical method is the simplest and most cost effective. In this thesis, electropolymerization and characterization of three different CPs namely poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI) and polypyrrole (PPy) and its copolymer, PEDOT/PANI and PEDOT/PPy were studied. The effect of applied potentials, E_p (1.0 V to 2.0 V *vs*. Ag/AgCl) and monomer concentrations (1 mM, 5 mM and 10 mM) on prepared polymers films were investigated.

The electrochemical polymerization of EDOT, ANI and Py were performed potentiostatically at different E_p for 5 minutes in aqueous solution in the presence of lithium perchlorate ($LiClO_4$) as supporting electrolyte. A new approach was used to perform the electrochemical copolymerization process of EDOT with ANI and EDOT with Py. The copolymer film was prepared at the potential obtained from the intercept points in the forward scan of cyclic voltammetry of the both corresponding monomers. A series of copolymer films were also electropolymerized at different EDOT/ANI and EDOT/Py concentration ratios at different E_p in aqueous solution containing $LiClO_4$.

The FTIR and Raman spectra confirmed the formation of homopolymers and copolymers. While, the morphology studies showed different structures of homopolymer and copolymers were obtained at different concentrations and E_p. The electrochemical properties of the resultant polymer films were further analyzed using cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS). High specific capacitance and low charge transfer resistances, R_{ct} were obtained for films with

globular structures. The impedance studies of these films show lower R_{ct} at E_p of 2.0 V. Electrochemical studies for copolymers revealed that specific capacitance and R_{ct} values are significantly affected after the incorporation of ANI (or Py) into EDOT. Few equivalent circuit models were used to fit the impedance spectra of homopolymers and copolymer where the spectra were fitted well.

The morphologies and electrochemical properties of the homopolymers and copolymer are significantly influence by monomer concentration and E_p. Based on the work reported in this thesis, the comparative studies of FTIR and Raman spectroscopy, scanning electron microscopy (SEM), CV and EIS for PEDOT, PANI and PPy films illustrate that the films shows adherent and homogenous morphologies as well good electrochemical properties at 1.0 V and 10 mM conditions.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PEMPOLIMERAN SECARA ELEKTROKIMIA DAN PENCIRIAN BAGI POLI(3,4-ETILENADIOKSITIOFENA), POLIANILINA, POLIPIROL DAN KOPOLIMERNYA

Oleh

SHALINI KULANDAIVALU

November 2015

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Beberapa tahun kebelakangan ini, polimer konduktif sering digunakan sebagai bahan asas dalam pelbagai aplikasi baru seperti sensor, sel solar dan peranti paparan elektrokronik. Antara kaedah yang digunakan untuk menyediakan polimer konduktif, kaedah elektrokimia adalah kaedah yang paling mudah dan menjimatkan kos. Dalam tesis ini, pempolimeran secara elektrokimia dan pencirian bagi tiga polimer konduktif yang berlainan iaitu poli(3,4-etilenadioksitiofena) (PEDOT), polyanilina (PANI) dan polipirol (PPy) dan kopolimer, PEDOT/PANI dan PEDOT/PPy telah dikaji. Kesan keupayaan, E_p (1.0 V to 2.0 V *vs.* Ag/AgCl) dan kepekatan monomer (1 mM, 5 mM and 10 mM) terhadap filem polimer telah dikaji.

Pempolimeran elektrokimia bagi EDOT, ANI dan Py telah dijalankan secara potentiostatik pada E_p yang berbeza selama 5 minit dalam larutan akueus yang mengandungi litium peklorat sebagai elektrolit sokongan. Satu pendekatan baru telah diperkenalkan untuk menjalankan proses pengkopolimeran elektrokimia EDOT dengan ANI dan EDOT dengan Py. Filem kopolimer telah dihasilkan pada E_p yang diperolehi daripada titik persilangan kitar ke depan dalam voltametri berkitar bagi kedua-dua monomer berkenanan. Kopolimer filem juga telah dihasilkan melalui pempolimeran elektrokimia pada nisbah kepekatan EDOT/ANI dan EDOT/Py yang berbeza pada E_p yang berlainan dalam larutan akueus yang mengandungi $LiClO_4$.

Kesemua spektrum Fourier spektroskopi inframerah (FTIR) dan Raman telah mengesahkan penghasilan homopolimer dan kopolimer. Manakala, kajian morfologi menunjukan penghasilan homopolimer dan kopolimer dengan kepelbagaian struktur yang diperolehi pada keupayaan dan kepekatan yang berlainan. Sifat elektrokimia bagi filem polimer yang diperolehi telah dianalisis seterusnya mengunakan teknik voltametri berkitar dan spektroskopi impedansi elektrokimia. Nilai kapasiti tinggi dan rintangan permindahan caj, R_{ct} yang rendah telah diperolehi bagi filem polimer yang mempunyai struktur globular. Kajian impedansi bagi polimer filem yang dihasilkan pada E_p 2.0 V menunjukkan nilai R_{ct} yang rendah. Kajian elekrokimia memberikan

kesan terhadap nilai kapasiti dan nilai R_{ct} apabila ANI (atau Py) digabungkan dengan EDOT. Beberapa model litar telah digunakan untuk disesuaikan dengan spektrum impedans bagi homopolimer dan kopolimer.

Morfologi dan sifat elecktrokimia bagi polimer dan kopolimer dipengaruhi oleh kepekatan monomer dan E_p. Berdasarkan kerja yang dilaporkan dalam tesis ini, kajian perbandingan bagi FTIR, spektroskopi Raman, mikroskopi imbasan elektron (SEM), CV dan EIS untuk PEDOT, PANI dan PPy filem menunjukkan filem yang dihasilkan pada 1.0 V dan 10 mM mempunyai morfologi permukaan yang homogen dan melekat kuat pada elektrod serta sifat elektrokimia yang baik.

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"Appreciation is a wonderful thing. It makes what is excellent in others belong to us as well."
~Voltaire ~

I certify that a Thesis Examination Committee has met on 05 November 2015 to conduct the final examination of Shalini Kulandaivalu on her thesis entitled "Electropolymerization and Characterization of Poly(3,4-ethylenedioxythiophene), Polyaniline, Polypyrrole and Their Copolymer" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF SYMBOLS

Symbol	Meaning	Usual unit
a	Area of electrode	cm^2
C	Capacitance	mF/cm^2
CPE	Constant phase element	F
E	Electrode potential	V
E_{op}	Onset potential	V
E_p	Applied potential	V
I	Current	A
R_{ct}	Charge transfer resistance	Ω
R_s	Solution resistance	Ω
S	Enclosed area in the CV curve	AV
t	Time	s
ΔU	Potential window	V
υ	Scan rate	V/s
χ^2	Chi squared	-
Z'	Real impedance	Ω
Z''	Imaginary impedance	Ω
Z_w	Warburg impedance	Ω

LIST OF ABBREVIATION

AC	alternating current
ANI	aniline
ATR	attenuated total reflection
BTB	1,4-bis(2-thienyl)benzene
CA	chronoamperometry
CB	conduction band
CE	counter electrode
CP	conducting polymer
CPE	constant phase element
CV	cyclic voltammetry
DC	direct current
EB	emeraldine base
EDL	electrical double layer
EDOT	3,4-ethylenedioxythiophene
EDOT/ANI	3,4-ethylenedioxythiophene/ aniline
EDOT/Py	3,4-ethylenedioxythiophene/ pyrrole
EIS	electrochemical impedance spectroscopy
FTIR	Fourier transforms infrared spectroscopy
HOMO	highest occupied molecular orbital
ICP	intrinsically conducting polymer
In	indole
ITO	indium tin oxide coated glass
kΩ	kilo ohms
kHz	kilohertz
LEB	leucoemeraldine base
LSV	linear sweep voltammetry
LUMO	lowest unoccupied molecular orbital
M	molar
mA	milli ampere
mF/cm^2	millifarad per centimetre square
mM	millimolar
mV	millivolt
nm	nanometer
OCP	open circuit potential
PA	polyacetylene
PAB	perningraniline base
PANI	polyaniline
PEDOT	poly(3,4-ethylenedioxythiophene)

PEDOT/PANI	poly(3,4 ethylenedioxythiophene)/ polyaniline copolymer
PEDOT/PPy	poly(3,4-ethylenedioxythiophene)/ polypyrrole copolymer
PP	polypropylene
PPP	polyparaphenylene
PPV	polyparaphenylene vinylene
PPy	polypyrrole
PSS	polystyrene sulfonate
PTh	polythiophene
Py	pyrrole
RE	reference electrode
SDS	sodium dodecylsulfate
SEM	scanning electron microscopy
VB	valence band
V	volts
WE	working electrode
1 mM PEDOT (1.0 V)	1 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.0 V
1 mM PEDOT (1.3 V)	1 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.3 V
1 mM PEDOT (1.5 V)	1 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.5 V
1 mM PEDOT (1.7 V)	1 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.7 V
1 mM PEDOT (2.0 V)	1 mM EDOT solution containing $LiClO_4$ electropolymerized at 2.0 V
5 mM PEDOT (1.0 V)	5 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.0 V
5 mM PEDOT (1.3 V)	5 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.3 V
5 mM PEDOT (1.5 V)	5 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.5 V
5 mM PEDOT (1.7 V)	5 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.7 V
5 mM PEDOT (2.0 V)	5 mM EDOT solution containing $LiClO_4$ electropolymerized at 2.0 V

10 mM PEDOT (1.0 V)	10 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.0 V
10 mM PEDOT (1.3 V)	10 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.3 V
10 mM PEDOT (1.5 V)	10 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.5 V
10 mM PEDOT (1.7 V)	10 mM EDOT solution containing $LiClO_4$ electropolymerized at 1.7 V
10 mM PEDOT (2.0 V)	10 mM EDOT solution containing $LiClO_4$ electropolymerized at 2.0 V
1 mM PANI (0.7 V)	1 mM ANI solution containing $LiClO_4$ electropolymerized at 0.7 V
1 mM PANI (1.0 V)	1 mM ANI solution containing $LiClO_4$ electropolymerized at 1.0 V
1 mM PANI (1.3 V)	1 mM ANI solution containing $LiClO_4$ electropolymerized at 1.3 V
1 mM PANI (1.5 V)	1 mM ANI solution containing $LiClO_4$ electropolymerized at 1.5 V
1 mM PANI (1.7 V)	1 mM ANI solution containing $LiClO_4$ electropolymerized at 1.7 V
1 mM PANI (2.0 V)	1 mM ANI solution containing $LiClO_4$ electropolymerized at 2.0 V
5 mM PANI (0.7 V)	5 mM ANI solution containing $LiClO_4$ electropolymerized at 0.7 V
5 mM PANI (1.0 V)	5 mM ANI solution containing $LiClO_4$ electropolymerized at 1.0 V
5 mM PANI (1.3 V)	5 mM ANI solution containing $LiClO_4$ electropolymerized at 1.3 V
5 mM PANI (1.5 V)	5 mM ANI solution containing $LiClO_4$ electropolymerized at 1.5 V
5 mM PANI (1.7 V)	5 mM ANI solution containing $LiClO_4$ electropolymerized at 1.7 V

5 mM PANI (2.0 V)	5 mM ANI solution containing $LiClO_4$ electropolymerized at 2.0 V
10 mM PANI (0.7 V)	10 mM ANI solution containing $LiClO_4$ electropolymerized at 0.7 V
10 mM PANI (1.0 V)	10 mM ANI solution containing $LiClO_4$ electropolymerized at 1.0 V
10 mM PANI (1.3 V)	10 mM ANI solution containing $LiClO_4$ electropolymerized at 1.3 V
10 mM PANI (1.5 V)	10 mM ANI solution containing $LiClO_4$ electropolymerized at 1.5 V
10 mM PANI (1.7 V)	10 mM ANI solution containing $LiClO_4$ electropolymerized at 1.7 V
10 mM PANI (2.0 V)	10 mM ANI solution containing $LiClO_4$ electropolymerized at 2.0 V
1 mM PPy (1.0 V)	1 mM Py solution containing $LiClO_4$ electropolymerized at 1.0 V
1 mM PPy (1.3 V)	1 mM Py solution containing $LiClO_4$ electropolymerized at 1.3 V
1 mM PPy (1.5 V)	1 mM Py solution containing $LiClO_4$ electropolymerized at 1.5 V
1 mM PPy (1.7 V)	1 mM Py solution containing $LiClO_4$ electropolymerized at 1.7 V
1 mM PPy (2.0 V)	1 mM Py solution containing $LiClO_4$ electropolymerized at 2.0 V
5 mM PPy (1.0 V)	5 mM Py solution containing $LiClO_4$ electropolymerized at 1.0 V
5 mM PPy (1.3 V)	5 mM Py solution containing $LiClO_4$ electropolymerized at 1.3 V
5 mM PPy (1.5 V)	5 mM Py solution containing $LiClO_4$ electropolymerized at 1.3 V
5 mM PPy (1.7 V)	5 mM Py solution containing $LiClO_4$ electropolymerized at 1.7 V

5 mM PPy (2.0 V)	5 mM Py solution containing $LiClO_4$ electropolymerized at 2.0 V
10 mM PPy (1.0 V)	10 mM Py solution containing $LiClO_4$ electropolymerized at 1.0 V
10 mM PPy (1.3 V)	10 mM Py solution containing $LiClO_4$ electropolymerized at 1.3 V
10 mM PPy (1.5 V)	10 mM Py solution containing $LiClO_4$ electropolymerized at 1.5 V
10 mM PPy (1.7 V)	10 mM Py solution containing $LiClO_4$ electropolymerized at 1.7 V
10 mM PPy (2.0 V)	10 mM Py solution containing $LiClO_4$ electropolymerized at 2.0 V
1 mM PEDOT /1 mM PANI (1.24 V)	1 mM EDOT and 1 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.24 V
1 mM PEDOT /5 mM PANI (1.25 V)	1 mM EDOT and 5 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.25 V
1 mM PEDOT/10 mM PANI (1.77 V)	1 mM EDOT and 10 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.77 V
5 mM PEDOT/1 mM PANI (1.08 V)	5 mM EDOT and 1 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.08 V
5 mM PEDOT/5 mM PANI (1.08 V)	5 mM EDOT and 5 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.08 V
5 mM PEDOT/10 mM PANI (1.12 V)	5 mM EDOT and 10 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.12 V
10 mM PEDOT/1 mM PANI (1.05 V)	10 mM EDOT and 1 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.05 V
10 mM PEDOT/5 mM PANI (1.06 V)	10 mM EDOT and 5 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.06 V

10 mM PEDOT/10 mM PANI (1.07 V)	10 mM EDOT and 10 mM ANI monomer solution mixture containing $LiClO_4$ electropolymerized at 1.07 V
1 mM PEDOT/1 mM PPy (1.15 V)	1 mM EDOT and 1 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.15 V
1 mM PEDOT/5 mM PPy (1.79 V)	1 mM EDOT and 5 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.79 V
5 mM PEDOT/5 mM PPy (1.06 V)	5 mM EDOT and 5 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.06 V
5 mM PEDOT/10 mM PPy (1.06 V)	5 mM EDOT and 10 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.06 V
5 mM PEDOT/10 mM PPy (1.13 V)	5 mM EDOT and 10 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.13 V
5 mM PEDOT/10 mM PPy (1.74 V)	5 mM EDOT and 10 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.74 V
10 mM PEDOT/5 mM PPy (1.04 V)	10 mM EDOT and 5 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.04 V
10 mM PEDOT/10 mM PPy (1.15 V)	10 mM EDOT and 10 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.15 V
10 mM PEDOT/10 mM PPy (1.59 V)	10 mM EDOT and 10 mM Py monomer solution mixture containing $LiClO_4$ electropolymerized at 1.59 V

CHAPTER 1

INTRODUCTION

1.1 Background

In this modern world, polymers and electronic devices are the two words interrelated with each other. Polymers often related with insulators or in other words, electrical conductance in polymers has been regarded as absurd phenomenon. However, the discovery of polyacetylene (PA), an electrically conductive polymer in 1977 (Chiang *et al.*, 1977) led to a new perception to polymer world. Over the last three decades, varies conducting polymers (CPs) have been explored by the research community. The CPs also known as synthetic metals have been the important subject of studies in the interdisciplinary fields in science and technology. Particularly, the CPs are widely utilized as a material of choice for various potential applications due to its combination of the metal-like conductance (electronic features) with the polymeric properties (Tat'yana and Oleg, 1997, Wanekaya *et al.*, 2006).

Amongst the family of CPs known to date, poly (3, 4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI) and polypyrrole (PPy) were captured the intense research effort of the world scientists. Being a derivative of polythiophene, PEDOT has become the foremost π- conjugated polymer gained the recent research interest due to its high conductivity about 300 S/cm (Groenendaal *et al.*, 2000), low bandgap approximately 1.6 eV (Pigani *et al.*, 2004) and good stable upon oxidation (Pigani *et al.*, 2004, Wang, 2009). On the other hand, PANI exhibits several advantages, namely good environmental stability, good electrical conductivity and thermal stability (Bhadra *et al.*, 2009). Whereas, due to its rich attractive properties, such as high conductivity, excellent environmental stability, good redox reversibility and ease of synthesis (Garcia-Cruz *et al.*, 2015, Kupila and Kankare, 1994, Yalçınkaya *et al.*, 2010) PPy still remained as the most extensively explored CPs. PPy is a very stable polymer in aqueous and non-aqueous solution exhibiting low oxidation potential compared with other CPs (Patois *et al.*, 2005).

1.2 Problem statement

Owning to the good properties of these polymers, the copolymerization of the monomers, aniline (ANI) or pyrrole (Py) with 3, 4-ethylenedioxythiophene (EDOT) may lead to the new copolymers with great properties. By definition, copolymerization is a process of combination of different monomers to obtain a new copolymer with better properties comparable with the monomers. Indeed, a major work has been focused on the electrochemical copolymerization of EDOT with different monomers to synthesize the copolymer with interesting properties. However, it is worth noting that most of the electrochemical copolymerization of EDOT were attempted in the presence of organic solvents such as acetonitrile and propylene carbonate or surfactants (Hu *et al.*, 2012, Nie *et al.*, 2008, Varis *et al.*, 2007, Zhang *et al.*, 2010) due to low solubility (2.1 g/l at 20 ^{o}C) of EDOT monomer in the aqueous solution (Qi and G. Pickup, 1998). Regardless, water still an appropriate choice for the polymerization media considering the environmental concern and economical issue. However, there were no studies reported on the copolymerization of EDOT monomer in the aqueous media without organic solvents or surfactants. Thus, this is the forcing force to study in details on the electrochemical copolymerization of the EDOT monomer with Py monomer (or with ANI monomer) in the aqueous medium with the absence of organic solvents or surfactants. Moreover, the differences in oxidation potential of the monomers determine the possibilities of the copolymerization. In present study, the onset potentials of the EDOT and Py are almost identical, whereas onset potentials of the EDOT and ANI are varies much. Therefore, incorporation of EDOT with ANI (and with Py) is achieved by using a new approach of copolymerization process to produce copolymer with the combination of the properties of both monomers.

1.3 Research Objectives

The ultimate goal of this thesis is to study and compare the properties of electropolymerized PEDOT, PANI, PPy films and their copolymer films. The objectives of this research are:

1. To prepare PEDOT, PANI, PPy, and their copolymers, PEDOT/PANI and PEDOT/PPy films via electropolymerization using chronoamperometry technique in aqueous solution containing perchlorate ion (ClO_4^-) on ITO electrodes
2. To evaluate the physical and electrochemical properties of the resulting conducting polymer films using scanning electron microscopy (SEM), Fourier transform infrared (FTIR), Raman spectroscopy, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).
3. To study the effect of applied potential and concentration of monomers on the properties of prepared homopolymer (PEDOT, PANI and PPy) and copolymers (PEDOT/PANI and PEDOT/PPy)

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