

# Synthesis and Characterization of Poly{2-[3-(1*H*-pyrrol-2-yl)phenyl]-1*H*-pyrrole} and Its Copolymer with EDOT<sup>1</sup>

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Received July 29, 2010

**Abstract**—A pyrrole-functionalized monomer 2-[3-(1*H*-pyrrol-2-yl)phenyl]-1*H*-pyrrole (PyPhPy) was synthesized. The structure of monomer was investigated by Nuclear Magnetic Resonance (<sup>1</sup>H NMR) and Fourier Transform Infrared (FTIR) spectroscopy. The chemical polymerization of PyPhPy (CPyPhPy) was realized using FeCl<sub>3</sub> as the oxidant. The electrochemical oxidative polymerization of polymer P(PyPhPy) and its copolymer with 3,4-ethylenedioxythiophene poly(2-[3-(1*H*-pyrrol-2-yl)phenyl]-1*H*-pyrrole-co-3,4-ethylenedioxythiophene) [P(PyPhPy-co-EDOT)] were achieved via potentiodynamic method by using NaClO<sub>4</sub>/LiClO<sub>4</sub> as the supporting electrolyte in CH<sub>3</sub>CN. Characterizations of the resulting polymers were performed by cyclic voltammetry (CV), FTIR, scanning electron microscopy (SEM), UV–Visible spectrophotometry (UV–Vis) and thermogravimetry analyses (TGA). Electrical conductivity of CPyPhPy, P(PyPhPy), and P(PyPhPy-co-EDOT) were measured by four-probe technique.

**DOI:** 10.1134/S1070363211120164

## INTRODUCTION

The search for organic conducting polymers has started in 1970s and up to date is largely focused on polyfuran [1], polythiophene [2–5], polypyrrole, and their derivatives [6]. The ability to dope conjugated polymers electrochemically is significant due to the easy combination of synthesis and characterization methods. Many applications of conjugated polymers, such as light emitting electrochemical cells [7, 8], microactuators [9, 10], energy storage [11], photovoltaic [12] and electrochromic devices (ECDs) [13–17], and sensors [18] are based on electrochemical transition between doped and neutral states or rely on the stability of a specific doping level.

Polypyrrole (PPy) is one of the well-known conjugated heterocyclic polymers having high

conductivity and environmental stability. It has been considered for use in many applications, including high energy batteries, electrochromic devices, and modified electrodes [19]. A number of procedures have been proposed to prepare polypyrrole composites to improve the mechanical properties of polypyrrole. PPy as a conductive polymer was electrochemically synthesized for the first time by Weiss et al. in 1965 [20] and later was extensively studied by Diaz [21]. Conductive and free-standing films were obtained by potentiostatic anodic polymerization of pyrrole. Many research efforts also have been dedicated to obtaining stable, processable, and conductive polymeric materials. Several composites of conducting polymers have been prepared for the simple reason of having polymers with good thermal and physical characteristics. In some cases, grafting between the insulating and the conducting polymers has also been observed to a certain extent [22–24].

<sup>1</sup> The article was submitted by the authors in English.

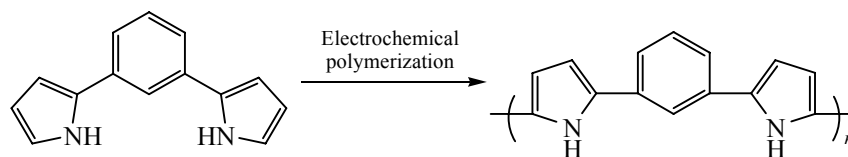


Fig. 1. Synthesis of P(PyPhPy).

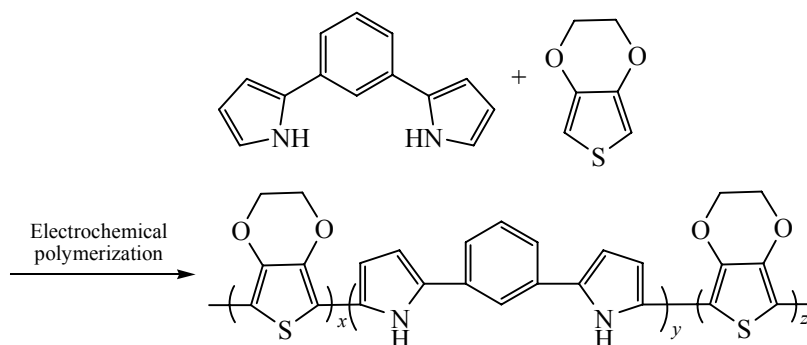


Fig. 2. Synthesis of copolymers of PyPhPy with EDOT.

In 1991, Jonas et al. [25] synthesized 3,4-ethylenedioxythiophene (EDOT) by locking the 3- and 4-positions of thiophene with an ethylenedioxy group yielding a highly electron-rich fused heterocycle which had low oxidation potential and was free from the possible  $\alpha$ ,  $\beta$  and  $\beta$ ,  $\beta$  linkages. Poly(3,4-ethylenedioxythiophene) (PEDOT) exhibits an optical band gap of 1.6 eV. Doped PEDOT is almost transparent in the visible region, and the neutral polymer is dark blue. Thus, this material is significant for its cathodically coloring electrochromic properties in device applications [26].

In the present work, 2-[3-(1H-pyrrol-2-yl)phenyl]-1H-pyrrole was for the first time synthesized as a monomer.  $^1\text{H-NMR}$  and FT-IR were used to analyze the structure of pyrrole derivative. The polymer (CPyPhPy) synthesized via chemical oxidative method was characterized by FT-IR. The electrochemical oxidative polymerization [P(PyPhPy)] of the monomer and its copolymer with 3,4-ethylenedioxythiophene [P(PyPhPy-co-EDOT)] were performed via potentiodynamic method by using  $\text{NaClO}_4/\text{LiClO}_4$  as the supporting electrolyte in  $\text{CH}_3\text{CN}$ . Characterizations of the resulting polymers were performed by CV, FT-IR, SEM, UV-Vis, and TGA. Electrical conductivity of CPyPhPy, P(PyPhPy), P(PyPhPy-co-EDOT), and PEDOT were measured by the four-probe technique.

## EXPERIMENTAL

Nitromethane (Aldrich), iron(III)chloride (Fluka), methanol (Merck), NaOH (Merck), phosgene (20% solution in toluene) (Aldrich), N,N-dimethylformamide (DMF) (Aldrich), tetrahydrofuran (THF) (Aldrich), 3,4-ethylenedioxythiophene (EDOT) (Aldrich), potassium tert-butoxide (Merck), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) (Merck), chloroform (Aldrich), silica gel (Merck), dichloromethane (DCM) (Merck), hexane (Merck) were used as received. The electrolysis solvent, acetonitrile ( $\text{CH}_3\text{CN}$ ) (Merck) was used without further purification. The supporting electrolytes, tetrafluoroammonium tetrahexafluoroborate (Merck), sodium perchlorate ( $\text{NaClO}_4$ ) (Aldrich), and lithium perchlorate ( $\text{LiClO}_4$ ) (Aldrich) were used as received.

The monomer was characterized using  $^1\text{H NMR}$  spectra (Bruker-Instrument-NMR Spectrometer DPX-400) recorded at  $25^\circ\text{C}$  using deuterated  $\text{CDCl}_3$  as solvent. The FTIR spectra were recorded on JASCO FT/IR-300E spectrometer. The FTIR spectra were recorded using KBr pellets in the range  $4000\text{--}400\text{ cm}^{-1}$ . UV-visible spectra were taken using DCM as the solvent on a Shimadzu MultiSpec-1501 instrument. Cyclic voltammograms were recorded in  $\text{NaClO}_4$  (0.1 M) and  $\text{LiClO}_4$  (0.1 M)/ $\text{CH}_3\text{CN}$  electrolyte-

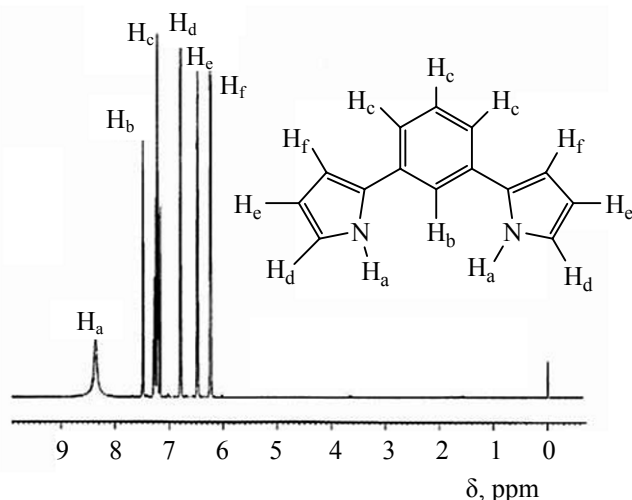


Fig. 3.  $^1\text{H}$  NMR spectrum of PyPhPy.

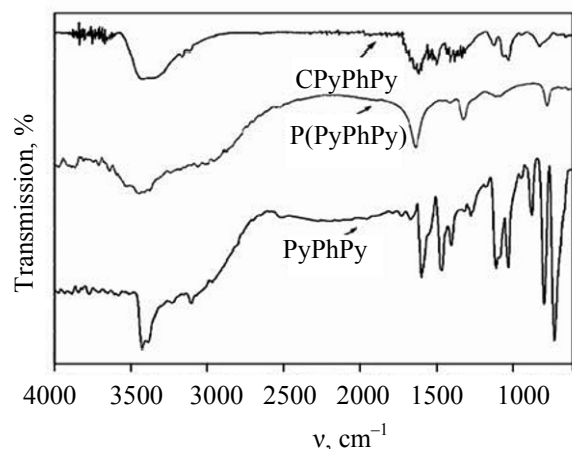


Fig. 4. FT-IR spectrum of PyPhPy, P(PyPhPy) and CPyPhPy.

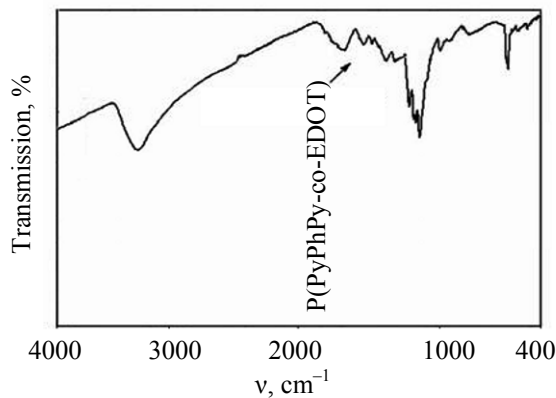


Fig. 5. FT-IR spectrum of P(PyPhPy-co-EDOT).

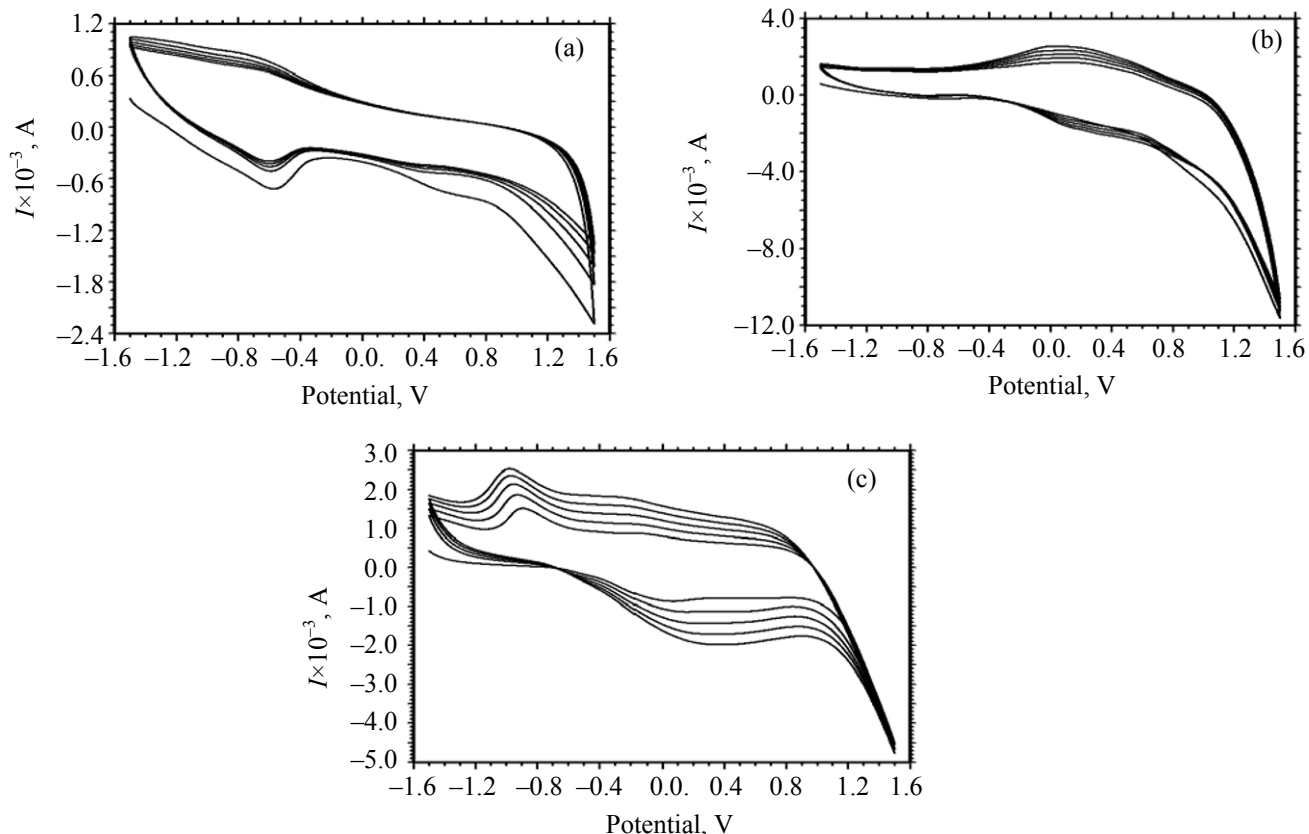
solvent couple with a system consisting of a potentiostat (CH Instruments 600) and a CV cell containing Pt-flake working electrode, Pt counter electrode, and a Ag wire pseudo reference electrode. Measurements were carried out at room temperature. Thermogravimetric analyses were performed between 25 and 1100°C under nitrogen at a heating rate of 5°C min<sup>-1</sup> using Perkin-Elmer Pyrisdiamond 6.0 model TG/DTA. The particle morphology of the polymer films was examined by means of scanning electron microscopy (Leo 440) operated at 20 kV. Electrical conductivity of the polymer was measured at room temperature by using four probe technique with a custom made instrument.

#### Synthesis of 2-[3-(1*H*-pyrrol-2-yl)phenyl]-1*H*-pyrrole (PyPhPy).

2-[3-(1*H*-pyrrol-2-yl)phenyl]-1*H*-pyrrole was prepared according to the published procedure [27]. A mixture of *N,N'*-diallylisophthaldiamide (2.44 g, 10 mmol), phosgene (20% solution in toluene, 40 ml), and DMF (4 drops) were stirred under argon atmosphere for 15 h at room temperature. The resulting mixture was then heated to 40–45°C for 2 h, after which the solvent was removed in vacuo (caution: phosgene is highly toxic and must be handled with care). The residue was dissolved in THF (60 ml) and added dropwise with stirring to a solution of potassium *tert*-butoxide (5.89 g, 52 mmol) in THF (60 ml) at 5–10°C under argon. After stirring for 1 h at this temperature, the reaction mixture was poured into ice water and extracted with chloroform (3×100 ml). The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to dryness. The residue was subjected to column chromatography (silicagel, dichloromethane eluent) to give crude product, which upon recrystallization from dichloromethane/hexane afforded PyPhPy in the form of a white solid. This compound was soluble in acetone, chloroform, THF, DMSO, acetonitrile, and dichloromethane (mp 163°C);  $^1\text{H}$  NMR (CDCl<sub>3</sub>),  $\delta$ : 6.21 d ( $J = 2.8$  Hz, 2H; Hf), 6.48 t (2H; He), 6.80 d (2H; Hd), 7.30–7.39 m (3H; Hc), 7.52 t ( $J = 1.6$  Hz, 1H; Hb), 8.40 s (2H; Ha); UV-Vis  $\lambda_{\text{max}}$  (nm) in dichloromethane: 585, 407.

#### Synthesis of polymer by chemical polymerization.

PyPhPy (1×10<sup>-3</sup> M) was dissolved in nitromethane (15 ml). Iron (III) chloride (2×10<sup>-3</sup> M) was dissolved in 15 ml of nitromethane and placed in a three-neck flask. Monomer solution was added dropwise to the iron (III) chloride solution at 0°C. The reaction was carried out for 5 min with constant stirring. The dark black product was first washed with



**Fig. 6.** Cyclic voltammograms of (a) PyPhPy, (b) PyPhPy in the presence of EDOT, and (c) EDOT, on a Pt-flake working electrode in 0.1 M LiClO<sub>4</sub>/NaClO<sub>4</sub>/CH<sub>3</sub>CN at 500 mV s<sup>-1</sup> scan rate.

methanol, filtered and then neutralized with 30% NaOH. This compound was insoluble in organic solvents.

**Electrochemical polymerization of PyPhPy.** Preparative electrochemical polymerization was performed by sweeping the potential between -1.5 V and +1.5 V with 500 mV s<sup>-1</sup> scan rate. 50 mg PyPhPy were dissolved in CH<sub>3</sub>CN and NaClO<sub>4</sub> (0.1 M) and LiClO<sub>4</sub> (0.1 M) were used as the supporting electrolyte (Fig. 1). Electrolyses were carried out using Pt working and counter electrodes and an Ag wire reference electrode at room temperature for 1 h. The free standing films were washed with CH<sub>3</sub>CN several times to remove unreacted monomer and the electrolyte.

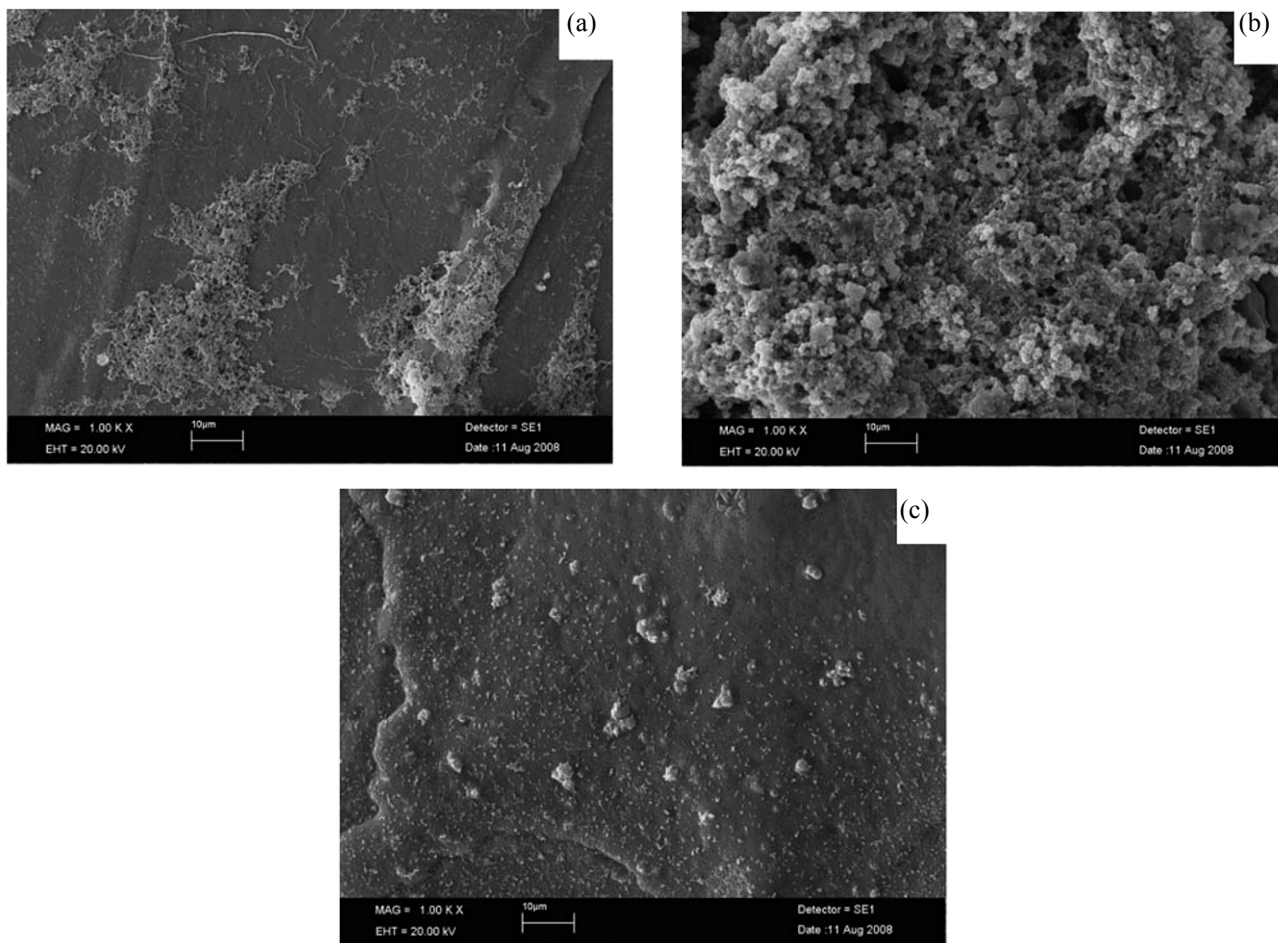
**Synthesis of conducting copolymer of PyPhPy with EDOT.** For the synthesis of conducting copolymer P(PyPhPy-co-EDOT), EDOT was used as the comonomer (Fig. 2). PyPhPy (1.3 × 10<sup>-3</sup> M) was dissolved in 0.1 M NaClO<sub>4</sub>/LiClO<sub>4</sub> in CH<sub>3</sub>CN and 1.3 × 10<sup>-3</sup> M of EDOT was introduced into a single compartment electrolysis cell. A three-electrode cell

assembly was used where the working electrode was a Pt-flake, the counter electrode was a platinum wire, and the Ag wire electrode was used as the pseudo reference.

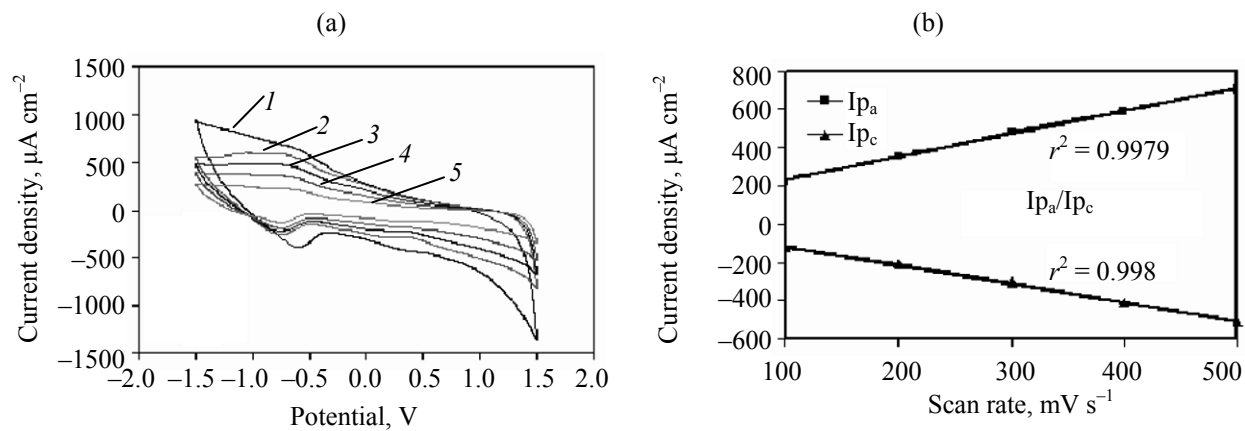
In a previous research Nakazaki et al. [28] have synthesized the 2-[3-(1H-pyrrol-2-yl)phenyl]-1H-pyrrole monomer with a different method and achieved the oxidative chemical polymerization of the monomer. In our study, we have synthesized the polymer and its copolymer with 3,4-ethylenedioxythiophene [P(PyPhPy-co-EDOT)] by electrochemical polymerization route.

<sup>1</sup>H NMR spectrum of PyPhPy is given in Fig. 3, δ<sub>H</sub>, ppm, (chloroform): 6.21 d (*J* = 2.8 Hz, 2H; Hf), 6.48 t (2H; He), 6.80 d (2H; Hd), 7.30–7.39 m (3H; Hc), 7.52 t (*J* = 1.6 Hz, 1H; Hb), 8.40 s (2H; Ha).

FT-IR spectrum of the PyPhPy shows the following absorption peaks: 3410 cm<sup>-1</sup> (N-H), 3107 cm<sup>-1</sup> (C-H<sub>α</sub> stretching of pyrrole), 2973 cm<sup>-1</sup> (aromatic C-H), 1599–1406 cm<sup>-1</sup> (aromatic C=C stretching due to



**Fig. 7.** SEM micrograph of (a) P(PyPhPy), (b) PEDOT, and (c) P[(PyPhPy)-co-EDOT].



**Fig. 8.** (a) Cyclic voltammogram of P(PyPhPy-co-EDOT) in monomer-free at different scan rates, mV s<sup>-1</sup>: (1) 500, (2) 400, (3) 300, (4) 200, and (5) 100. (b) Anodic and cathodic peak currents as a function of the scan rate.

pyrrole and benzene),  $730\text{ cm}^{-1}$  ( $\text{C-H}_\alpha$  out of plane bending of pyrrole) (Fig. 4).

Most of the characteristic peaks of the monomer PyPhPy remained unperturbed upon chemical polymerization. The intensity absorption bands of the monomer at  $3107\text{ cm}^{-1}$  and  $730\text{ cm}^{-1}$  arising from  $\text{C-H}_\alpha$  stretching vibrations of pyrrole moiety disappeared completely. This is an evidence of the polymerization at the 2,5 positions of pyrrole moiety of the monomer. The broad band observed at around  $1614\text{ cm}^{-1}$  proves the presence of polyconjugation (Fig. 4).

FTIR spectra of electrochemically synthesized P(PyPhPy) showed the characteristic peaks of the monomer. The peaks related to  $\text{C-H}_\alpha$  stretching vibrations of pyrrole disappeared completely. The new broad band at around  $1641\text{ cm}^{-1}$  was due to polyconjugation. The strong absorption peak at  $1119\text{ cm}^{-1}$  and  $632\text{ cm}^{-1}$  was attributed to the incorporation of  $\text{ClO}_4^-$  ions into the polymer film during doping process (Fig. 4).

After the electrochemical copolymerization of PyPhPy with EDOT, the disappearance of peaks at  $730$  and  $3107\text{ cm}^{-1}$  evidence the polymerization through 2,5 positions of pyrrole ring. The shoulder observed at  $1645\text{ cm}^{-1}$  is due to the conjugation and the peak at  $1144\text{ cm}^{-1}$ , due to  $\text{C-O-C}$  group, indicates that EDOT is incorporated into the polymer matrix. The peaks appeared at  $1089$ ,  $1113$  and  $632\text{ cm}^{-1}$  show the presence of the dopant ion,  $\text{ClO}_4^-$  (Fig. 5).

Cyclic voltammogram of PyPhPy in  $\text{CH}_3\text{CN}/\text{LiClO}_4\text{-NaClO}_4$  solvent/electrolyte couple indicated an oxidation peak at  $-0.50\text{ V}$  and a reduction peak at  $-0.65\text{ V}$ . When the range between  $-1.5\text{ V}$  and  $+1.5\text{ V}$  (Fig. 6a) was scanned, it was observed that the electroactivity increased with increasing scan number.

To investigate the copolymer we performed CV studies in the presence of EDOT under the same experimental conditions. There was a drastic change in the voltammogram, both the current increase between consecutive cycles and the oxidation potential of the material were different from those of PyPhPy and EDOT (Fig. 6c), which in fact, could be interpreted as the formation of copolymer (Fig. 6b).

SEM micrographs of P(PyPhPy) (Fig. 7a) imply that the synthesized monomer is good for film forming. SEM micrograph of P(PyPhPy-co-EDOT) (Fig. 7c) was different from both P(PyPhPy) and PEDOT (Fig. 7b). This difference could be attributed to copolymerization.

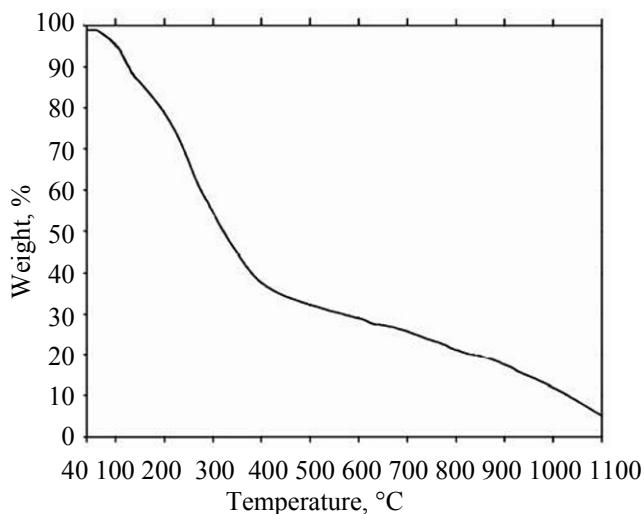


Fig. 9. TGA curve of P(PyPhPy).

P(PyPhPy-co-EDOT) film was prepared via constant potential electrolysis. Its redox switching in monomer free electrolyte revealed a single, well-defined redox process (Fig. 8a) as shows the cyclic voltammogram of P(PyPhPy-co-EDOT) at different scan rates. The current responses were directly proportional to the scan rate indicating that the polymer film was electroactive and well adhered to the electrode [29]. The linear scan rate dependence with respect to current for the anodic and cathodic peaks up to  $500\text{ mV s}^{-1}$  is illustrated in Fig. 8b.

Electrical conductivity of the P(PyPhPy) and CPyPhPy materials were measured at room temperature by using four probe technique with a custom-made instrument. Pellets of the P(PyPhPy) and CPyPhPy for conductivity measurement were prepared in a hydraulic press. The conductivities of electrochemically and chemically prepared polymers were measured as  $1.7 \times 10^{-4}\text{ S cm}^{-1}$  and  $4.5 \times 10^{-5}\text{ S cm}^{-1}$  respectively via four probe technique. The conductivity of electrochemically prepared homopolymer was  $4.5 \times 10^{-5}\text{ S cm}^{-1}$ ; whereas P(PyPhPy-co-EDOT) film was measured as  $2.5 \times 10^{-3}\text{ S cm}^{-1}$ . Introducing EDOT into the polymer chain increased the conductivity.

TGA of P(PyPhPy) was measured under nitrogen atmosphere in the temperature range  $25\text{--}1100^\circ\text{C}$  in order to investigate the thermal stability. The 5% weight loss of the polymer was revealed at  $110^\circ\text{C}$ , 50% weight loss at  $320^\circ\text{C}$ , and according to the TGA result, the carbonaceous residue values of P(PyPhPy) was 10% at  $1020^\circ\text{C}$  (Fig. 9).

## CONCLUSIONS

P(PyPhPy) and CPyPhPy were synthesized by both chemical and electrochemical oxidative polymerizations. The homopolymer of PyPhPy was also synthesized potentiodynamically in CH<sub>3</sub>CN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1 M) solvent–electrolyte couple. The conductivities of P(PyPhPy) and CPyPhPy were measured as  $1.7 \times 10^{-4}$  S cm<sup>-1</sup> and  $4.5 \times 10^{-5}$  S cm<sup>-1</sup> respectively. According to TGA results, the synthesized P(PyPhPy) polymer is stable against heat. The synthesis of copolymer from (2-[3-(1H-pyrrol-2-yl)phenyl]-1H-pyrrole) PyPhPy and EDOT was successfully achieved in CH<sub>3</sub>CN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1 M) solvent–electrolyte couple. Copolymer was characterized by CV, SEM and FTIR studies. The conductivity of P(PyPhPy-co-EDOT) was measured as  $2.5 \times 10^{-3}$  S cm<sup>-1</sup>. Scan rate dependence of the peak currents measurements show that the current responses were directly proportional to the scan rate.

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