

Synthesis and Characterization of Conducting Copolymers of Quinoxaline Derivatives

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Received 28 January 2010; accepted 28 August 2010

DOI 10.1002/app.33317

Published online 1 December 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Electrochemical copolymerizations of 2,3-di(2-thienyl)quinoxaline (M1), 6-methyl-2,3-di(2-thienyl)quinoxaline (M2), and 2,3-di(2-thienyl)quinoxaline-6-yl-(phenyl)methanone (M3) with 3,4-ethylenedioxy thiophene (EDOT) were carried out in CH₃CN/TBABF₄ (0.1M) solvent-electrolyte couple via potentiodynamic electrolysis. The obtained copolymers were characterized by cyclic voltammetry (CV), Fourier transform-infrared spectroscopy

(FTIR), scanning electron microscopy (SEM), and thermogravimetry analyses (TGA). The conductivity measurements of copolymers and PEDOT were performed by the four-probe technique. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1713–1719, 2011

Key words: momomers; synthesis; copolymerization; NMR; thermogravimetric analysis (TGA)

INTRODUCTION

Conducting polymers have received considerable attention in recent years due to their attractive practical applications. Among these polymers, a great deal of work has been devoted to polyheterocycles such as polypyrrole and polythiophene.^{1–4} In 1991, Jonas and Schrader⁵ 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 has low oxidation potential and is free from the possible α , β and β , β 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.⁶

The structural diversity and biological importance of nitrogen containing heterocycles have made them attractive synthetic targets for many years. Moreover, these compounds are found in various natural sources.⁷ Quinoxaline based oligothiophene copolymers have served as electron transport conjugated polymers for electroluminescent devices in the field of macromo-

lecules.⁸ Many quinoxaline derivatives have displayed photoluminescence and electroluminescence properties. Compounds with fused quinoxaline aromatic rings are used as components in organic light-emitting devices and optoelectronic devices.^{9,10} and several quinoxaline based oligothiophene copolymers have displayed electrochromic properties.^{11,12} Moreover, quinoxaline systems have also been used in the development of novel organic dyes and organic semiconductors.¹³

In this context, numerous investigations have focused on the synthesis of polymers with low bandgap. Among low bandgap polymers, polymers containing both thiophene rings and nitrogen containing heterocycles have recently been reported.^{14,15} In particular, Kauffmann et al.¹⁶ reported the synthesis of 2,3-di(2-thienyl)quinoxaline, with 49% yield, while Hrdlovic et al.¹⁷ reported 89% yield. Diaz et al.¹⁸ obtained the monomer through a simple method of synthesis with 98% yield.

This study deals with the synthesis of quinoxaline derivative monomers 2,3-di(2-thienyl)quinoxaline (M1), 6-methyl-2,3-di(2-thienyl)quinoxaline (M2), and (2,3-di(2-thienyl)quinoxaline-6-yl)(phenyl)methanone (M3). Characterizations of these monomers were carried out with FT-IR and ¹H-NMR techniques. Copolymers were synthesized utilizing 3,4-ethylenedioxy thiophene (EDOT) as the comonomer by electrochemical polymerization. CH₃CN/TBABF₄ (0.1M) was used as the solvent/electrolyte couple. Structures of resultant copolymers were evaluated with CV, FT-IR, SEM, and TGA techniques. Redox behavior of the copolymers was also investigated via scan rate dependence studies. The conductivity of

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Contract grant sponsors: Research Foundation of Nigde University (FEB 2007-11) (Nigde-Turkey), TUBA.

the copolymers and PEDOT were also determined by the four-probe technique.

EXPERIMENTAL

Chemicals

Thiophene, oxalyl chloride, 1,2-phenyldiamine, 4-methyl-1,2-phenyldiamine, 3,4-diaminobenzophenone, 3,4-ethylenedioxythiophene, acetonitrile (CH₃CN), tetrabutylammonium tetrafluoroborate (TBABF₄), and *p*-toluenesulfonic acid (PTSA) were obtained from Aldrich. Sodium carbonate (Na₂CO₃), magnesium sulfate (MgSO₄), ethanol, dichloromethane (DCM), hydrochloric acid (HCl), aluminum chloride (AlCl₃), and silica gel were purchased from Merck. Toluene was purchased from Sigma. All reagents and solvents were of analytical grade and used without further purification.

Equipment

NMR spectra were recorded on a Bruker-Instrument NMR Spectrometer DPX-400 using CDCl₃ and DMSO-d₆ as the solvents. The FT-IR spectra were achieved on JASCO FT/IR-300E spectrometer using KBr discs (4000–400 cm⁻¹). Cyclic voltammograms were carried out in TBABF₄ (0.1M)/CH₃CN electrolyte-solvent couple with a system consisting of an electrochemical analyzer (CH Instruments 600) and a CV cell containing indium tin oxide (ITO)-coated glass or Pt plate as working electrode, Pt counter electrode, and an Ag wire pseudo reference electrode. The particle morphology of the copolymer films was examined by means of scanning electron microscopy (CARL-ZEISS EVO-40) operated at 20 kV. Thermogravimetric analyses were performed between 25 and 1000°C under nitrogen with a heating rate of 5°C.min⁻¹ using Perkin-Elmer Pyrisdiamond 6.0 model TG/DTA. Electrical conductivity of the copolymers and PEDOT was measured using the four-probe technique by a standard conductometer. All experiments were carried out at room temperature.

Synthesis of 1,2-di(2-thienyl)-1,2-ethanedione (TED)

The double Friedel-Crafts reaction, which was first suggested by Merz and Ellinger,¹⁹ was chosen. A suspension of AlCl₃ (16 g, 0.12 mol) in CH₂Cl₂ (15 mL) was added dropwise into a solution of thiophene (9.61 mL, 0.12 mol) and oxalyl chloride (4.20 mL, 0.05 mol) in CH₂Cl₂. The red mixture was stirred at room temperature for 4 h. The mixture was then quenched with ice and concentrated HCl (5 mL). After intensive stirring for 1 h the dark green organic phase was separated, washed by 2M HCl and H₂O NaHCO₃ solutions, respectively, and dried over

MgSO₄. After evaporation of the solvent a blue-green solid remained, which was suspended in ethanol. Filtration and washing with ethanol and diethyl ether provided a green solid. A green color solid was obtained in 78% yield. The synthetic route of 1,2-di(2-thienyl)-1,2-ethanedione is shown in Figure 1.

Synthesis of 2,3-di(2-thienyl)quinoxaline (M1)

The synthesis of 2,3-di(2-thienyl)quinoxaline (M1) was according to the procedure reported in previous studies.^{16–18} The monomer (M1) was synthesized with 1,2-di(2-thienyl)-1,2-ethanedione and 1,2-phenyldiamine in the presence of a catalytic amount of PTSA. A round-bottomed flask equipped with an argon inlet and a magnetic stirrer was charged with 1,2-di(2-thienyl)-1,2-ethanedione (1.11 g, 5 mmol), 1,2-phenyldiamine (0.76 g, 7 mmol), PTSA (0.095 g, 0.5 mmol), and toluene. The resulting mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene, followed by flash column chromatography (SiO₂ column, elution with dichloromethane), afforded the desired compound. A yellow color powder was obtained in 80% yield. The synthetic route of M1 is shown in Figure 1.

Synthesis of 6-methyl-2,3-di(2-thienyl)quinoxaline (M2)

The monomer (M2) was synthesized from 1,2-di(2-thienyl)-1,2-ethanedione and 4-methyl-1,2-phenyldiamine in the presence of a catalytic amount of PTSA. A round-bottomed flask equipped with an argon inlet and a magnetic stirrer was charged with 1,2-di(2-thienyl)-1,2-ethanedione (0.56 g, 2.5 mmol), 4-methyl-1,2-phenyldiamine (0.43 g, 3.5 mmol), PTSA (0.048 g, 0.25 mmol), and toluene. The resulting mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene, followed by flash column chromatography (SiO₂ column, elution with dichloromethane), afforded the desired compound. An orange color powder was obtained in 83% yield. The synthetic route of M2 is shown in Figure 1.

Synthesis of 2,3-di(2-thienyl)quinoxaline-6-yl(phenyl)methanone (M3)

The monomer (M3) was synthesized reacting 1,2-di(2-thienyl)-1,2-ethanedione with 3,4-diaminobenzophenone in the presence of a catalytic amount of PTSA. A round-bottomed flask equipped with an argon inlet and a magnetic stirrer was charged with 1,2-di(2-thienyl)-1,2-ethanedione (0.47 g, 2.13 mmol), 3,4-diaminobenzophenone (0.63 g, 3.0 mmol), PTSA (0.038 g, 0.2 mmol), and toluene. The resultant mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene, followed by flash

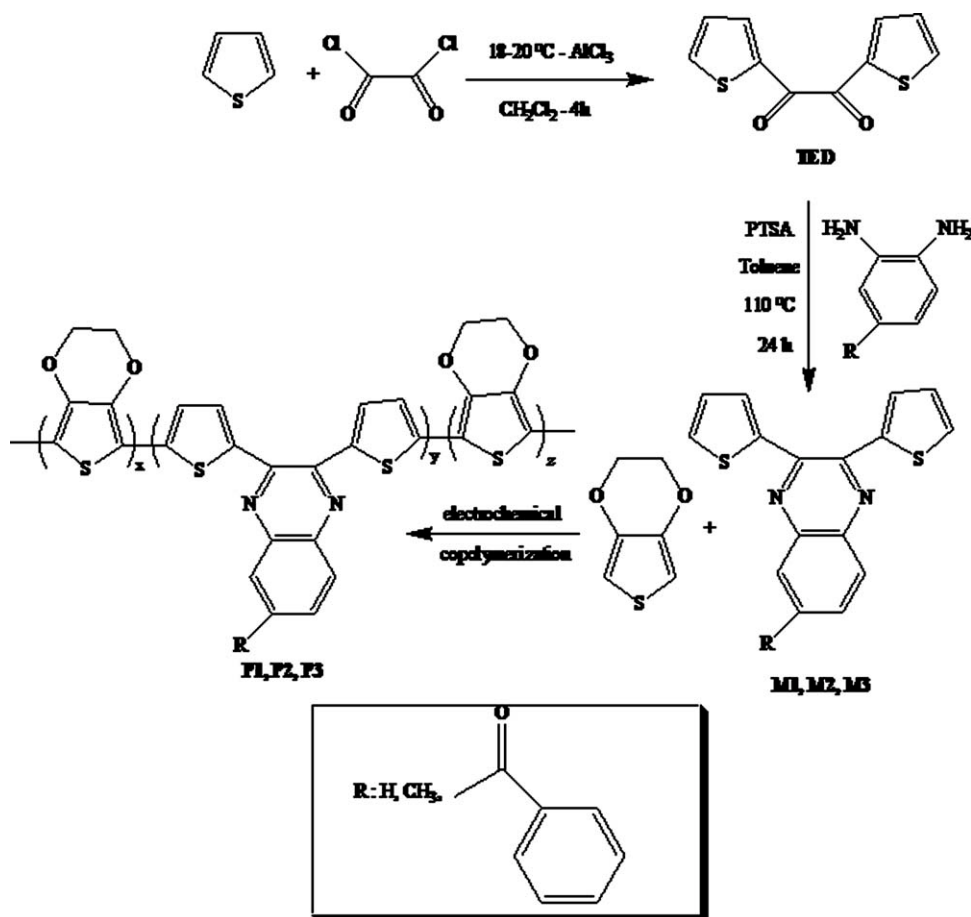


Figure 1 The synthetic route of 1,2-di(2-thienyl)-1,2-ethanedione, monomers and copolymers.

column chromatography (SiO_2 column, elution with dichloromethane), afforded the desired compound. A red color powder was obtained in 76% yield. The synthetic route of M3 is shown in Figure 1.

Synthesis of conducting copolymers with Edot

M1, M2, M3, and EDOT were used for synthesis of conductive copolymers (Fig. 1). M1, M2, and M3 (1.3×10^{-3} M) were dissolved in CH_3CN containing 0.1M TBABF_4 as electrolyte, and 1.3×10^{-3} M of EDOT was introduced into a single compartment electrolysis cell. A three-electrode cell assembly was used where the working electrode was an ITO-coated glass, while Pt flake was used as the counter and an Ag wire was used as the pseudo reference electrode. The copolymers were potentiodynamically deposited on ITO.

RESULTS AND DISCUSSION

In this study syntheses of three different quinoxaline derivative monomers were achieved. Copolymers of these monomers were synthesized via electrochemical method. Structures of these monomers and copolymers were characterized.

$^1\text{H-NMR}$ spectra

$^1\text{H-NMR}$ spectrum (in CDCl_3) of TED revealed three peaks that are 8.00 (2H, H-5 in thiophene), 7.77 (2H, H-3 in thiophene), and 7.14 (2H, H-4 in thiophene). While M1 (400 MHz, 25°C , in CDCl_3) showed five peaks: 8.01 (2H in quinoxaline), 7.66 (2H in quinoxaline), 7.43 (2H, H-5 in thiophene), 7.19 (2H, H-3 in thiophene), 6.97 (2H, H-4 in thiophene). Similarly, $^1\text{H-NMR}$ spectrum of M2 (in DMSO-d_6) displayed signals at 8.28 (2H in quinoxaline), 8.08 (1H in quinoxaline), 8.01 (2H, H-5 in thiophene), 7.32 (4H, H-3, and H-4 in thiophene), 3.41 (3H, CH_3) and M3 (in DMSO-d_6) at 8.30 (1H in quinoxaline), 8.11 (1H in quinoxaline), 8.06 (1H in quinoxaline), 8.01 (2H in benzene), 7.87 (1H in benzene), 7.72 (2H in benzene), 7.63 (2H, H-5 in thiophene), and 7.33 (4H, H-3, and H-4 in thiophene). These data are in accordance with the results obtained through FT-IR studies.

FT-IR spectra

The C-H stretching bands of thiophene moieties and the stretching of C = C bonds, azomethine group (C = N) are signified by the appearance of peaks around $3000-3100$ and $1500-1650$ cm^{-1} for all of the

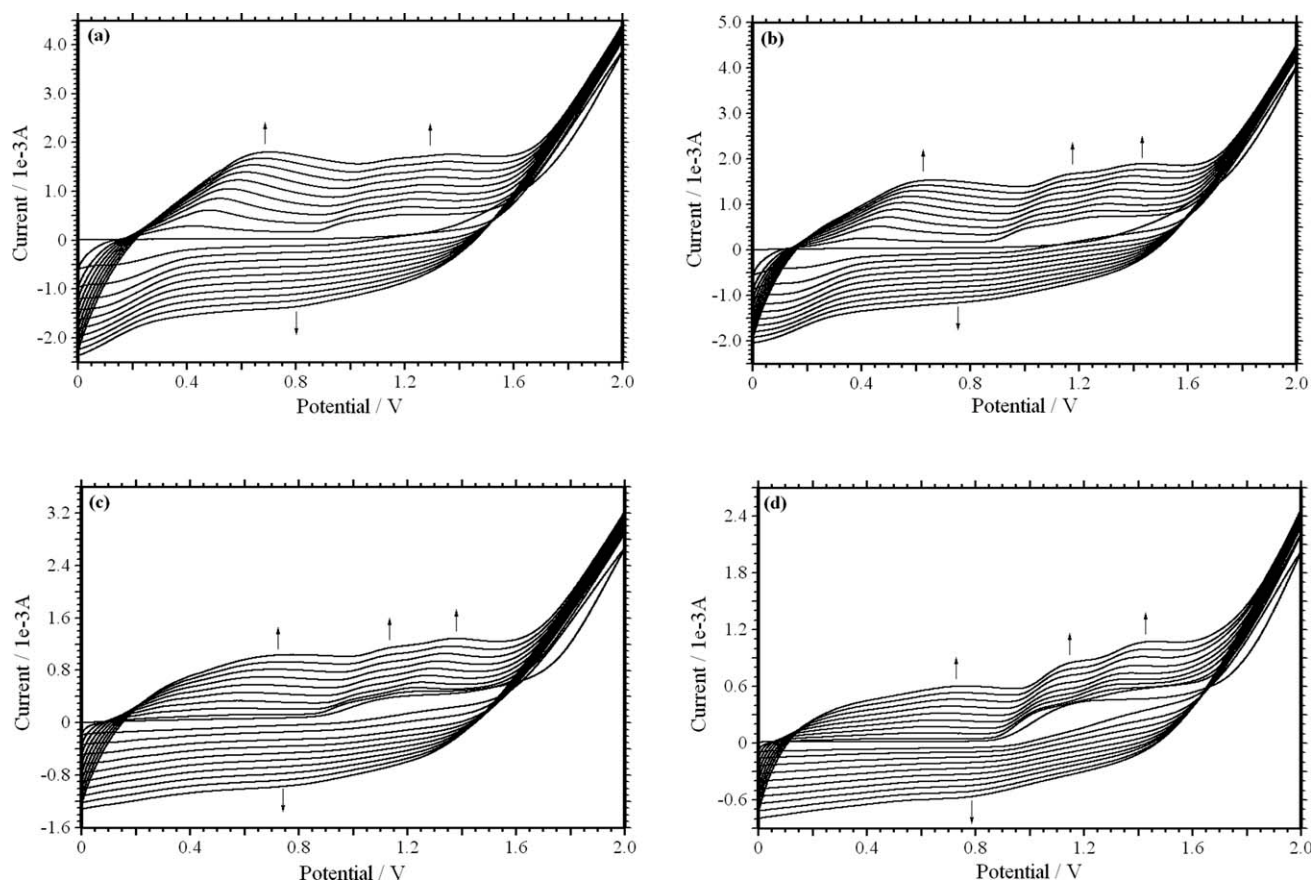


Figure 2 Cyclic voltammograms of (a) P1, (b) P2, (c) P3, and (d) PEDOT in 0.1M $\text{CH}_3\text{CN}/\text{TBABF}_4$ on a indium/tin oxide (ITO)-coated glass plate working electrode with 500 mVs^{-1} scan rate.

monomers. Moreover the aromatic C-H out-of plane bands appeared at 844 cm^{-1} , 864 cm^{-1} , and 871 cm^{-1} while the aromatic C-H in-plane emerged at 1046 , 1079 , 1089 cm^{-1} for monomers. Upon copolymerization, some of the characteristic peaks of the monomers remained unperturbed, while the peaks regarding C-H stretching and out of plane bending disappeared completely. Such observation is the evidence of polymerization through 2, 5 positions of the monomers. Presence of the new peak at 946 , 944 , and 943 cm^{-1} in FTIR spectra of copolymers P1, P2, and P3 respectively, is due to asymmetric C-O-C stretching of etheric units that stem from comonomer EDOT. Moreover, the broad band centered at 1600 cm^{-1} and the intense band at 1081 cm^{-1} revealed the formation of polyconjugation and presence dopant anion, respectively. Thus, existence of the characteristic peaks related to the monomers and the comonomer could be considered as a proof of copolymerization.^{20,21}

Cyclic voltammetry (CV)

Redox behavior of the monomers was investigated via CV in $\text{TBABF}_4/\text{ACN}$ system with ITO working electrode at a scan rate of 500 mVs^{-1} . Each of M1, M2, and

M3 monomers revealed two irreversible oxidation peaks at 1.41 , 1.62 V , 1.39 , 1.66 V and 1.31 , 1.70 V and one reversible reduction peak at -1.09 , -1.29 , and -1.25 V , respectively. Such observation is in accordance with the previous studies^{11,22} where the irreversible oxidation peaks are considered to be due to thiophene moieties and the reversible reduction behavior originates from quinoxaline moiety. However, upon repetitive potentiodynamic scans leakage of the homopolymer from the electrode surface was observed and none of monomers revealed neither homogeneous film coating on the electrode nor an increase in the electroactivity.

As a further step, copolymerization of M1, M2, and M3 were performed in the presence of EDOT. EDOT was utilized as the comonomer since it readily oxidizes at around 1.2 V (which is very close to the first oxidation peak potential of quinoxaline based monomers) and it rapidly forms film on the electrode. It is known that to ensure successful electrochemical copolymerization, both monomers should oxidize to form their reactive radical cations at approximately the same potential. A structural representation of the reaction taking place during electrochemical copolymerization is shown in Figure 1. Figure 2(a-d) displays potentiodynamic scans of M1 [Fig. 2(a)], M2

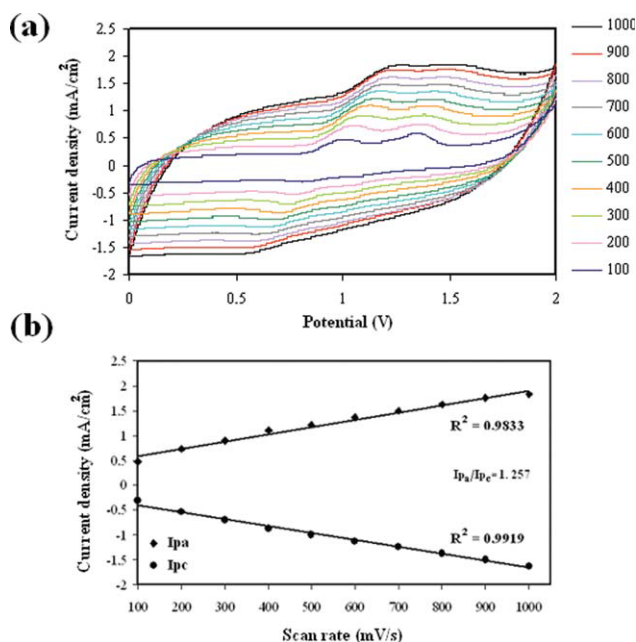


Figure 3 (a) Cyclic voltammograms of P1 in monomer-free $\text{CH}_3\text{CN}/\text{TBABF}_4$ solvent/electrolyte. (b) Peak current versus scan rate for P1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[Fig. 2(b)], M3 [Fig. 2(c)] in the presence of EDOT and pure EDOT [Fig. 2(d)] in $\text{TBABF}_4/\text{ACN}$ system with ITO working electrode at a scan rate of 500 mVs^{-1} . During potentiodynamic scan the anodic peaks of P1 appeared at 0.68 and 1.27 V while the cathodic peak emerged at 0.82 V. For the case of P2 the anodic peaks appeared at 0.62, 1.16, and 1.45 V while the cathodic peak emerged at 0.84 V. During copolymerization of M3 with EDOT, the anodic and cathodic peak potentials were recorded as 0.69, 1.14, and 1.29 V and 0.79 V, respectively. As seen in Figure 2 for all the systems, redox potentials of copolymers are clearly different from PEDOT and each other. Such result could be interpreted as an additional proof of true copolymer formation.

Redox activity of the conducting copolymers

To investigate the redox activity of the conducting copolymers, the polymer films were prepared via constant potential electrolysis on ITO working electrode and their switching characteristic were recorded in monomer free in $\text{TBABF}_4/\text{ACN}$ system. The cyclic voltammograms of P1, P2, and P3 at different scan rates were given in Figures 3(a), 4(a), and 5(a). The current responses were directly proportional to the scan rate indicating that the polymer films were electroactive and well adhered to the electrode.²³ The anodic and cathodic peak scan rate currents show a linear dependence as a function of the scan rate as illustrated in Figures 3(b), 4(b), and 5(b) for the cases of P1, P2, and P3. This demonstrates

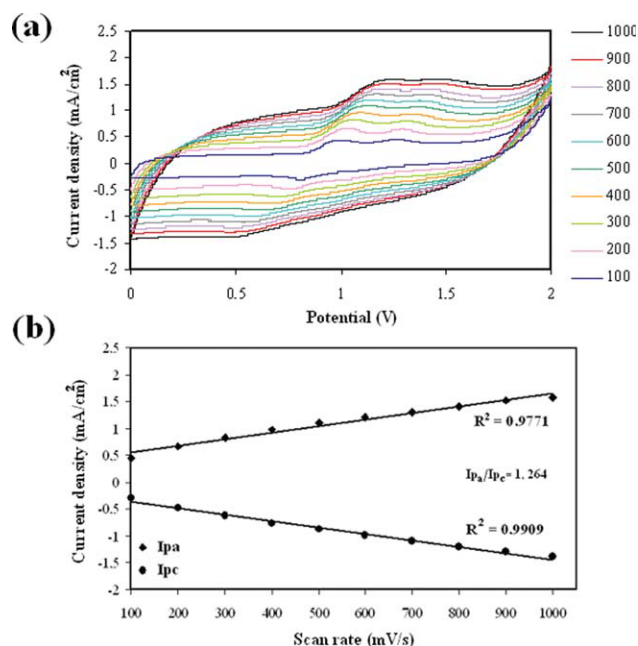


Figure 4 (a) Cyclic voltammograms of P2 in monomer-free $\text{CH}_3\text{CN}/\text{TBABF}_4$ solvent/electrolyte. (b) Peak current versus scan rate for P2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the electrochemical processes are not diffusion limited and reversible even at very high scan rates.

Morphology of films

The surface morphologies of synthesized P1 [Fig. 6(a)], P2 [Fig. 6(b)], P3 [Fig. 6(c)], and PEDOT

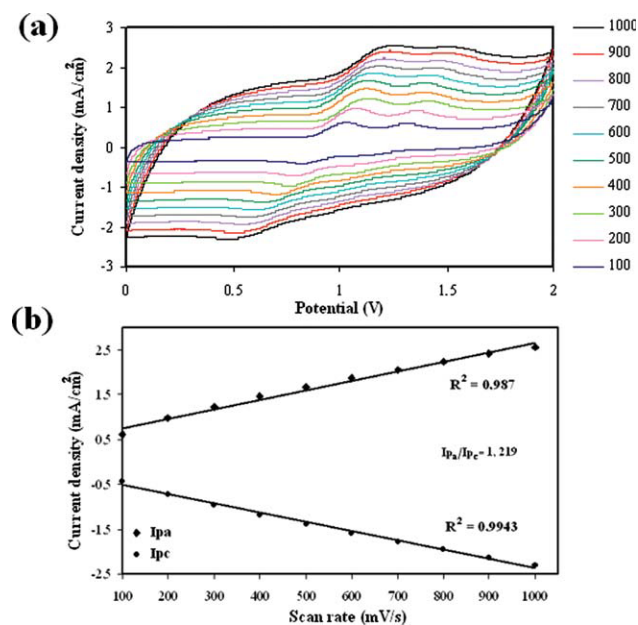


Figure 5 (a) Cyclic voltammograms of P3 in monomer-free $\text{CH}_3\text{CN}/\text{TBABF}_4$ solvent/electrolyte. (b) Peak current versus scan rate for P3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

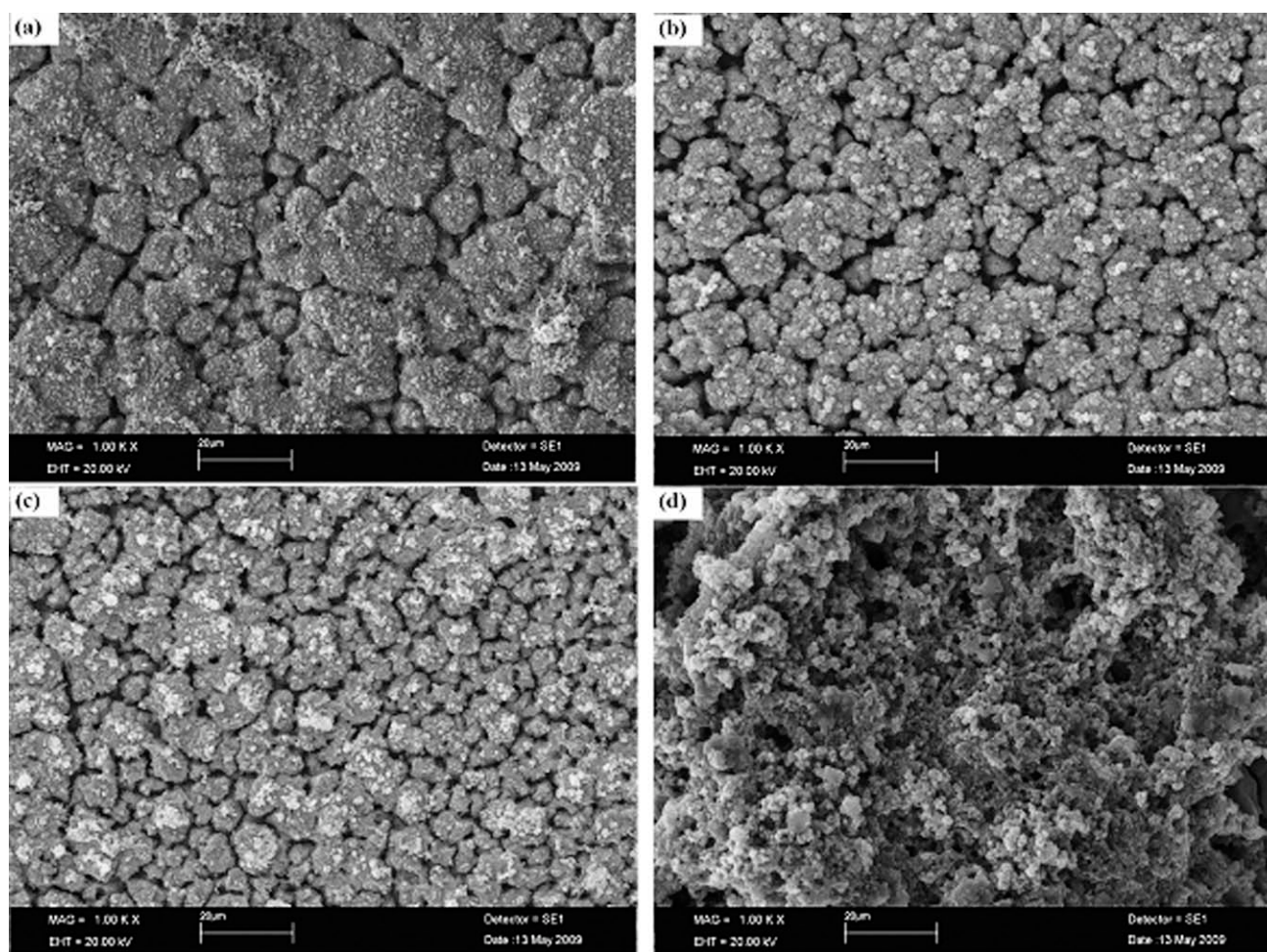


Figure 6 SEM micrographs of (a) P1, (b) P2, (c) P3, and (d) PEDOT (magnification $\times 1000$).

[Fig. 6(d)] were investigated using a scanning electron microscope. The samples were prepared by electrolysis with the sufficient thick films (*ca* 50 μm) on ITO electrode. SEM micrographs of copolymers imply that the synthesized monomers are good in film forming. Surface micrographs of all copolymers are in globular morphology where P2, and P3 are very similar to each other. This observation could be related to the monomer structure, where both M2 and M3 are substituent on their quinoxaline moieties. On the contrary PEDOT reveals a highly porous three-dimensional morphology under same electropolymerization conditions. Thus, SEM micrographs could be considered as a further proof of copolymerization.

Thermal analysis of copolymers

Thermal methods are interesting tools for determination of thermal stability and disintegration energy of polymers. Heating the polymers causes chemical and physical transformations that are accompanied by endothermic or exothermic processes.^{24,25} These

reactions are determined accurately by thermogravimetric analysis (TGA). In this study, thermogravimetric analysis was performed to understand the thermal stability of the copolymers that contain azomethine group on their backbone which is known to be susceptible to degradation. Therefore, P1, P2, P3, and PEDOT were subjected to analysis under nitrogen atmosphere in the temperature range from 25 to 1000°C and thermograms are provided on Table I. All copolymers reveals less than 5% weight loss up to 100°C which is known to be mainly related to the solvent removal. Hence, it could be inferred that these copolymers could find use in applications up to 100°C.

TABLE I
Thermal Decompositions of (I) P1, (II) P2, (III) P3, and (IV) PEDOT

| Compound | 5% Weight loss (°C) | 50% Weight loss (°C) | % Char residue at 1000°C |
|----------|---------------------|----------------------|--------------------------|
| P1 | 130 | 442 | 21.5 |
| P2 | 168 | 413 | 24.2 |
| P3 | 174 | 486 | 27.3 |
| PEDOT | 155 | 390 | 14.2 |

All copolymers displayed a second weight loss about 400°C originating due to dopant removal. This behavior is the characteristic of electrochemically synthesized conducting polymers and investigated through other studies.²⁶ Among the copolymers P3 displayed a distinctive stability revealing 27.3% char residue at 1000°C. While PEDOT has the lowest thermal stability with the % 14.2 char residue according to Table I.

Conductivity of the films

Electrical conductivities of the P1, P2, P3, and PEDOT materials were measured by four-probe technique at room temperature. The samples were prepared by electrolysis with the sufficient thick films (*ca* 50 μm) on ITO electrode. Electrical conductivity values of the P1, P2, and P3 were found to be 2.8×10^{-2} S/cm, 3.5×10^{-3} S/cm, and 4.2×10^{-3} S/cm, respectively. While the conductivity of pristine PEDOT was 1.0×10^{-2} S/cm.

CONCLUSIONS

Quinoxaline derivatives M1, M2, and M3 were successfully synthesized. Structures of the monomers were determined by ¹H-NMR and FT-IR techniques. Each of M1, M2 and M3 monomers revealed two irreversible oxidation peaks and one reversible reduction peak, respectively. Electrochemical polymerization of monomers and EDOT was achieved. The structures of P1, P2, and P3 were characterized using CV, FT-IR, SEM, and TGA techniques. The conductivities of copolymers and PEDOT were determined via four-probe techniques. Results of CV, FT-IR, and SEM studies showed that formation of true copolymers were achieved and the copolymers are distinct from PEDOT. The scan rate dependence of the peak current measurements shows that the current responses were directly proportional to the scan rate. This indicates that the electrochemical processes at the electrode was not diffusion limited and were reversible even at very high scan rates. The copolymers are electroactive and well adhered to the electrode.

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