

# Synthesis and characterization of new light-emitting copolymers containing 3,4-dialkoxythiophenes

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## Abstract

We report the synthesis, optical and electrochemical properties of a new series of polyoxadiazoles (**P1–P3**) consisting of 3,4-dialkoxythiophene and 1,4-divinylbenzene units. The polymers are prepared using the precursor polyhydrazide route. The polymers have well defined structure and exhibit good thermal stability with the onset decomposition temperature in nitrogen at around 330 °C. The optical and charge-transporting properties of the polymers are investigated by UV–vis spectroscopy, fluorescence emission spectroscopy and cyclic voltammetry. The UV–vis absorption spectra of polymers in solution showed a maximum at around 380 nm. The polymers depicted bluish-green fluorescence in solutions and green fluorescence in thin films. Cyclic voltammetry studies reveal that these copolymers have low-lying LUMO energy levels ranging from 3.25 to 3.31 eV and HOMO energy levels ranging from 5.48 to 5.56 eV, which indicated that the polymers are expected to provide enhanced charge-transporting (electron transport/hole blocking) properties for the development of efficient polymer light-emitting diodes (PLEDs). © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Conjugated polymers; Polycondensation; Fluorescence; Light-emitting diodes

## 1. Introduction

Conducting polymers have been the subject of considerable academic and industrial research due to their wide range of applications like light-emitting diodes (LEDs), electrochromic devices, field effect transistors and solar cells [1–9]. In the last decade, great efforts have been devoted to the design and synthesis of light-emitting polymers for the fabrication of polymer light-emitting diodes (PLEDs). A number of conjugated polymers including poly(paraphenylenevinylene) (PPV) [10,11], poly(paraphenylene) (PPP) [12,13], polythiophene (PT) [14,15] and polyfluorene (PF) [16] have been widely used as light-emitting materials in devices. However, one major problem with these polymers is that they are  $\pi$ -excessive in nature and hence are much better at accepting and transporting holes than electrons. Another series of polymers containing  $\pi$ -deficient heterocycles like pyridine, pyran, and oxadiazoles show greater tendency to

transport electrons than holes [17]. It is necessary to balance the injection and transport of electrons and holes to achieve high device efficiencies. For most of the conjugated polymers, the barrier between the LUMO of the polymer and the work function of the cathode is much larger than that between the HOMO of the polymer and the work function of the anode that results in an imbalance of the injection between electrons and holes. Utilization of low work function metals like Ca or Li as cathode [18] or insertion of an electron transporting/hole blocking layer between the emitter and cathode [19] are the two strategies to improve the efficiency of the polymer LEDs. Another approach to improve the efficiency is to modify the chemical structure of the emitting polymer molecule, i.e. synthesis of new polymers with desired HOMO and LUMO levels. The most promising approach of adjusting the HOMO and LUMO levels of the conjugated polymers involves the incorporation of both n- and p-dopable segments into the polymer backbone. In this direction, few conjugated donor–acceptor copolymers constituted of  $\pi$ -excessive and  $\pi$ -deficient units were synthesized and showed unique electrochemical and optical properties [20–23]. 3,4-Dialkoxy substituted polythiophenes show facile dopability and lower band gap

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ascribe to the electron-donating nature of the alkoxy moiety. In addition, introduction of long alkoxy pendants at 3- and 4-positions of the thiophene ring improves the solvent processability of the corresponding polymer. On the other hand polyoxadiazoles, due to high electron affinity of the oxadiazole moiety are attractive candidates for electron transporting materials. Further, it has been reported that incorporation of vinylene linkages serve to planarize the polymer backbone by overcoming torsional interactions between rings that could serve to increase the band gap [24]. In this report, we describe the synthesis and characterization of a series of polyoxadiazoles containing 3,4-dialkoxythiophene and 1,4-divinylbenzene units in the polymer backbone.

## 2. Experimental part

### 2.1. Materials and instrumentation

Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**1**) was synthesized according to the literature procedure [25]. Dimethylformamide (DMF) and acetonitrile (ACN) were dried by distillation over  $\text{CaH}_2$ . Tetrabutylammoniumperchlorate (TBAPC) and *n*-bromoalkanes were purchased from Lancaster (UK) and were used as received. All other solvents and reagents were of analytical grade, were purchased commercially and used without further purification. Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates (**2a–c**) were synthesized starting from compound **1** according to the reported procedure [26–28]. 3,3'-(1,4-Phenylene)bis[2-propenoyl chloride] (**6**) was synthesized following the reported procedure [29]. Infrared spectra of all intermediate compounds and polymers were recorded on a Nicolet Avatar 330 FT-IR (Thermo Electron Corporation). The UV–vis spectra of the polymers were measured using a Varian CARY 500 spectrophotometer. Thermogravimetric analysis (TGA) was carried out with a thermal analysis 2950 thermogravimetric analyzer (TA instruments).  $^1\text{H}$  NMR spectra were obtained with AMX 400 MHz FT-NMR spectrometer using TMS/solvent signal as internal reference. Fluorescence spectra of the polymers were recorded using a Perkin-Elmer LS 50B luminescence spectrometer. Elemental analyses were performed on a Flash EA 1112 CHNS analyzer (Thermo Electron Corporation). The electrochemical studies of the polymers were carried out using a AUTOLAB PGSTAT 30 electrochemical analyzer. Cyclic voltammograms were recorded using a three-electrode cell system, with a glass carbon button as working electrode, a Pt wire as counter electrode and an Ag/AgCl electrode as the reference electrode.

### 2.2. General procedure for the synthesis of 3,4-dialkoxythiophene-2,5-carbonyldihydrazide (**3a–c**)

Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylate (0.5 g) was added into a solution of 10 ml of hydrazine hydrate in 40 ml of methanol. The reaction mixture was refluxed for 2 h. Upon cooling the solution to room temperature a white precipitate was obtained. The precipitate was filtered, washed with petroleum ether and dried under vacuum to get the product as white solid.

3,4-Dihexyloxythiophene-2,5-carbonyldihydrazide (**3a**): yield: 90%,  $^1\text{H}$  NMR (DMSO- $d^6$ ) 8.82 (s, 2H), 4.58 (s, 4H), 4.13 (t, 4H), 1.2–1.8 (m, 16H), 0.88 (t, 6H). IR: 3408, 3328, 3293, 3197, 2931, 2862, 1652, 1507, 1369, 1307, 1057, 950, 631  $\text{cm}^{-1}$ . Elemental ( $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_4\text{S}$ ) calc: C, 54.27; H, 7.5; N, 14.07; S, 8.04. Found: C, 54.02; H, 7.73; N, 14.04; S, 7.99.

3,4-Dioctyloxythiophene-2,5-carbonyldihydrazide (**3b**): yield: 85%,  $^1\text{H}$  NMR (DMSO- $d^6$ ) 8.84 (s, 2H), 4.58 (s, 4H), 4.13 (t, 4H), 1.2–1.8 (m, 24H), 0.89 (t, 6H). IR: 3407, 3331, 3289, 3194, 2920, 2858, 1653, 1508, 1369, 1304, 1055, 948, 629  $\text{cm}^{-1}$ . Elemental ( $\text{C}_{22}\text{H}_{40}\text{N}_4\text{O}_4\text{S}$ ) calc: C, 57.9; H, 8.78; N, 12.28; S, 7.01. Found: C, 57.67; H, 8.77; N, 12.31; S, 6.64.

3,4-Didecyloxythiophene-2,5-carbonyldihydrazide (**3c**): yield: 95%,  $^1\text{H}$  NMR (DMSO- $d^6$ ) 8.9 (s, 2H), 4.6 (s, 4H), 4.12 (t, 4H), 1.3–1.8 (m, 32H), 0.93 (t, 6H). IR: 3410, 3331, 3292, 3194, 2919, 2853, 1655, 1507, 1370, 1303, 1056, 953, 625  $\text{cm}^{-1}$ . Elemental ( $\text{C}_{26}\text{H}_{48}\text{N}_4\text{O}_4\text{S}$ ) calc: C, 60.94; H, 9.44; N, 10.94; S, 5.64. Found: C, 60.87; H, 9.24; N, 10.75; S, 5.94.

### 2.3. General procedure for the synthesis of polyhydrazides (**7a–c**)

To a mixture of 1 equivalent of appropriate dihydrazide, 2 equivalent of anhydrous aluminum chloride and 0.1 ml of pyridine, 1 equivalent of the diacid chloride **6** was added slowly at room temperature. The reaction mixture was stirred at room temperature for 5 h. The resultant yellow solution was heated at 80 °C with stirring for 20 h. After cooling to room temperature the reaction mixture was poured into water to get a precipitate. The precipitate was collected by filtration and was washed with water followed by acetone and finally dried in oven to get the corresponding polyhydrazides in 70–85% yield.

**7a**: Yield: 80%, IR: 3325, 2954, 2872, 1646, 1593, 1509, 1434, 1304, 1052, 985, 832, 526  $\text{cm}^{-1}$ . **7b**: Yield: 85%, IR: 3325, 2949, 2873, 1664, 1624, 1508, 1305, 1233, 1115, 1047, 981, 828, 752, 509  $\text{cm}^{-1}$ . **7c**: Yield: 70%, IR: 3324, 2926, 2852, 1685, 1626, 1517, 1428, 1334, 1283, 1223, 1053, 980, 945, 830, 756, 679, 547  $\text{cm}^{-1}$ .

### 2.4. General procedure for the synthesis of polyoxadiazoles (**P1–P3**)

The mixture of polyhydrazide and 50 ml of polyphosphoric acid was heated at 100 °C for 5 h. The reaction mixture was then cooled to room temperature and poured into excess of water. The resulting precipitate was collected by filtration and was washed with water followed by acetone and dried in oven to get the polymers in 70–80% yield.

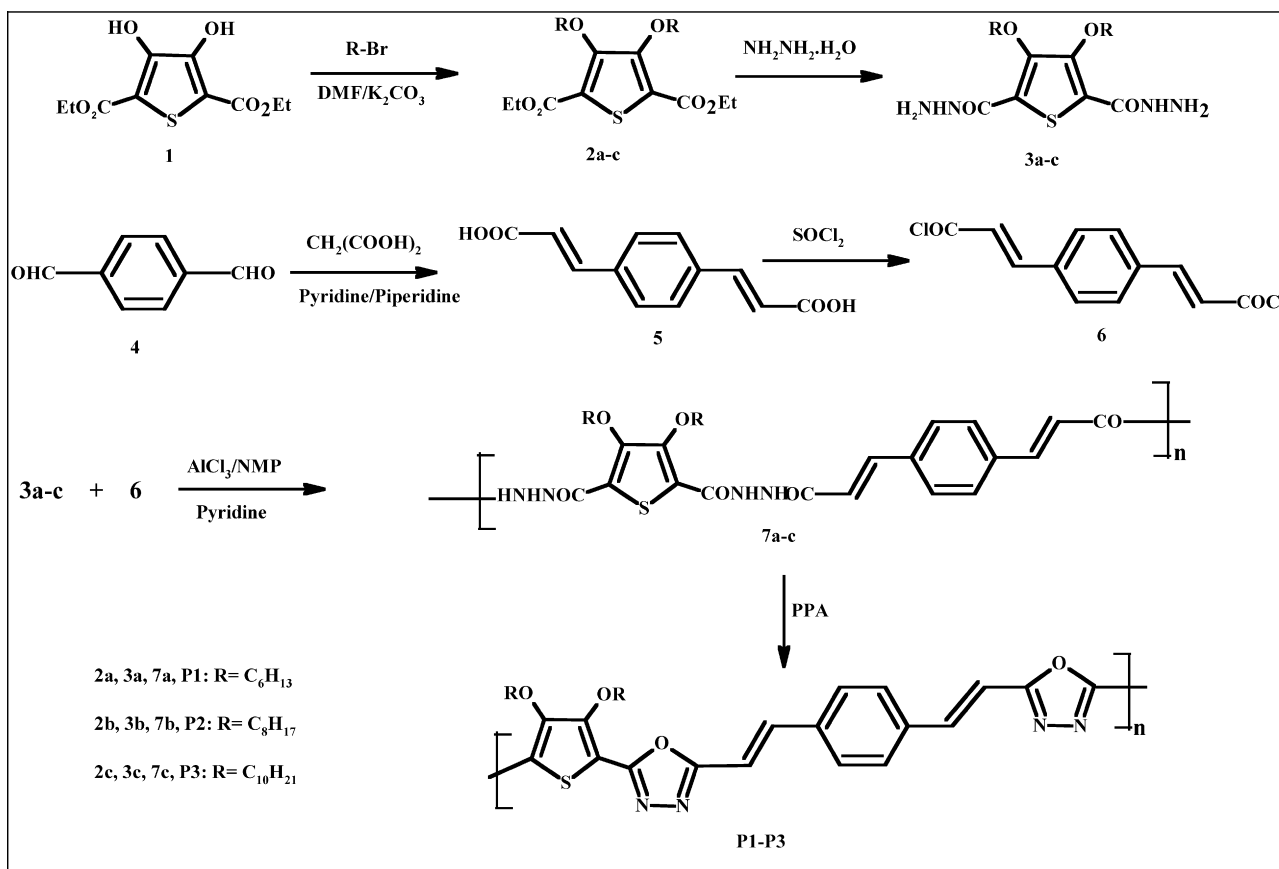
**P1**:  $^1\text{H}$  NMR (DMSO- $d^6$ ) 7.97–6.86 (m), 4.13 (t), 1.8–0.89 (m). IR: 2961, 2878, 1662, 1524, 1458, 1253, 1009, 965, 867, 734, 519  $\text{cm}^{-1}$ . **P2**:  $^1\text{H}$  NMR (DMSO- $d^6$ ) 7.9–6.74 (m), 4.12 (t), 1.8–0.88 (m). IR: 2956, 2873, 1664, 1525, 1456, 1207, 1006, 968, 814, 731, 524  $\text{cm}^{-1}$ . **P3**:  $^1\text{H}$  NMR (DMSO- $d^6$ ) 8.01–6.89 (m), 4.14 (t), 1.82–0.9 (m). IR: 2930, 2852, 1636, 1525, 1464, 1207, 1008, 970, 818, 730, 528  $\text{cm}^{-1}$ .

### 3. Results and discussion

#### 3.1. Synthesis and characterization of polymers

Scheme 1 shows the synthetic route to the synthesis of monomers and polymers. Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates (**2a–c**) were prepared by treating the compound **1** with corresponding *n*-bromoalkane in the presence of potassium carbonate and DMF. For the synthesis of 3,4-dialkoxythiophene-2,5-carbonyldihydrazides (**3a–c**), corresponding diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates were treated with excess of hydrazine monohydrate in methanol. 1,4-Benzenedicarboxaldehyde was treated with malonic acid (**4**) in pyridine in the presence of a catalytic amount of piperidine to give 3,3'-(1,4-phenylene)bis[2-propenoic acid] (**5**), which was then treated with excess thionyl chloride to obtain 3,3'-(1,4-phenylene)bis[2-propenoyl chloride] (**6**). Polyhydrazides (**7a–c**) were prepared by the polycondensation reaction of 3,3'-(1,4-phenylene)bis[2-propenoyl chloride] with the corresponding 3,4-dialkoxythiophene-2,5-carbonyldihydrazide in *N*-methylpyrrolidone (NMP) in the presence of anhydrous aluminum chloride and pyridine. As observed for other polyhydrazides these polyhydrazides are insoluble in common organic solvents at ambient and at elevated temperatures. The polyhydrazides were converted in to the corresponding poly (1,3,4-oxadiazole)s, (**P1–P3**), by cyclodehydration of the hydrazide

group into 1,3,4-oxadiazole ring, using polyphosphoric acid (PPA), which functions both as solvent and dehydrating agent. The polymers **P1–P3** were obtained as bluish-black powders. All the polymers are partially soluble in conventional solvents such as  $\text{CHCl}_3$  and THF, but readily soluble in DMF, DMSO, NMP, and in strong organic acids like trifluoroacetic acid. The FT-IR spectra of the polymers were consistent with their chemical structures. In particular, the FT-IR spectrum of **P2** showed characteristic absorptions at  $2956, 2873 \text{ cm}^{-1}$  (C–H stretching of aliphatic segments);  $1644, 1525 \text{ cm}^{-1}$  (1,3,4-oxadiazole ring);  $1207, 1006 \text{ cm}^{-1}$  (C–O–C stretching of ether bond and oxadiazole);  $1456, 968 \text{ cm}^{-1}$  (aromatic and CH=CH trans). The  $^1\text{H}$  NMR spectra of the polymers in  $\text{DMSO}-d_6$  displayed peaks at around  $\delta 8.01\text{--}6.74$  due to aromatic and vinylic protons, a triplet around  $\delta 4.1$  due to the  $-\text{OCH}_2-$  protons of the alkoxy groups on the thiophene ring. In addition, multiplet peaks were observed in the range  $\delta 1.8\text{--}0.9$ , due to  $-(\text{CH}_2)_n-$  protons of the alkoxy group. Thermogravimetric analysis of all oxadiazole polymers was carried out under nitrogen atmosphere at a heating rate of  $5^\circ\text{C}/\text{min}$ . All the polymers are found to be thermally stable up to  $\sim 330^\circ\text{C}$ . DSC studies were performed to observe glass transition temperature ( $T_g$ ) of the polymers. The samples were heated up to  $300^\circ\text{C}$  under nitrogen atmosphere at a heating rate of  $5^\circ\text{C}/\text{min}$ . No  $T_g$  or melting point was observed suggesting that the polymers are either having very high  $T_g$  or are highly crystalline in nature and decompose before melting.



Scheme 1. Synthesis of polymers.

Table 1  
UV–vis absorption maxima, emission maxima and fluorescence quantum yields of the polymers

Polymer	Absorption, $\lambda_{\max}$ (nm)	Emission, $\lambda_{\max}$ (nm)		Optical band gap, $E_g$ (eV)	Quantum yield <sup>a</sup> (%)
	Solution	Solution	Film		
P1	373	470	502	2.35	30
P2	378	474	506	2.24	26
P3	381	479	512	2.20	28

<sup>a</sup> Quantum yield relative to quinine sulfate.  $10^{-5}$  M quinine sulfate in 0.1 M  $H_2SO_4$ .

### 3.2. Optical properties

The UV–vis absorption and fluorescence spectra of the polymers were recorded both in solution and in thin film and the corresponding spectral data are summarized in Table 1. As shown in Fig. 1, the absorption maxima of the polymers in dilute DMF solutions (ca.  $10^{-5}$ ) are 373 nm for **P1**, 378 nm for **P2** and 381 nm for **P3**. In addition, the absorption spectra of the polymers displayed a shoulder at 306 nm. Compared with poly(3,4-dialkoxythiophenes), **P1–P3** showed a red shift in absorption spectra. This may be due to the presence of 1,4-divinylbenzene moiety in **P1–P3**, which serves to alleviate steric effects of the alkoxy groups in the adjacent thienylene rings. Hence, electron-donating contributions from the alkoxy groups to the electronic structure of the polymers become more prominent. The absorption spectra of the polymer thin films (Fig. 2) are rather broad and so their  $\lambda_{\max}$  values could not be precisely determined. However, their optical energy band gap ( $E_g$ ) was calculated from the absorption edge in the thin films to be 2.20–2.38 eV (Table 1). As shown in Fig. 3, the emissive maxima of the polymers in dilute DMF solutions (ca.  $10^{-5}$ ) are 470 nm for **P1**, 474 nm for **P2**, and 479 nm for **P3**. The Stokes shift determined to be 97, 96 and 98 nm for **P1**, **P2** and **P3**, respectively. The fluorescence emission spectra of these polymers in thin films are shown in Fig. 4. The polymers emit intense

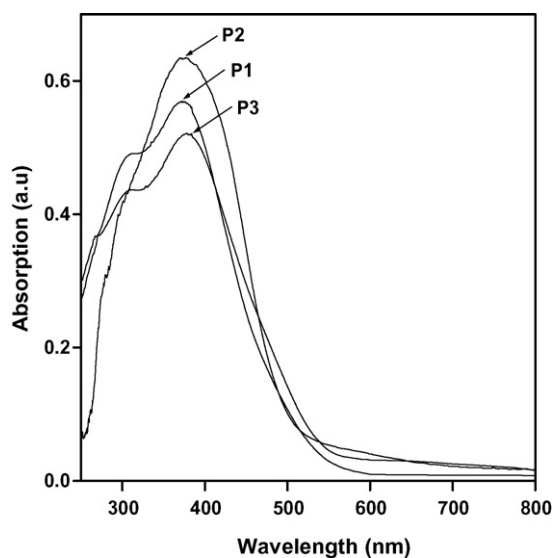


Fig. 1. UV–vis absorption spectra of P1–P3 in DMF solutions.

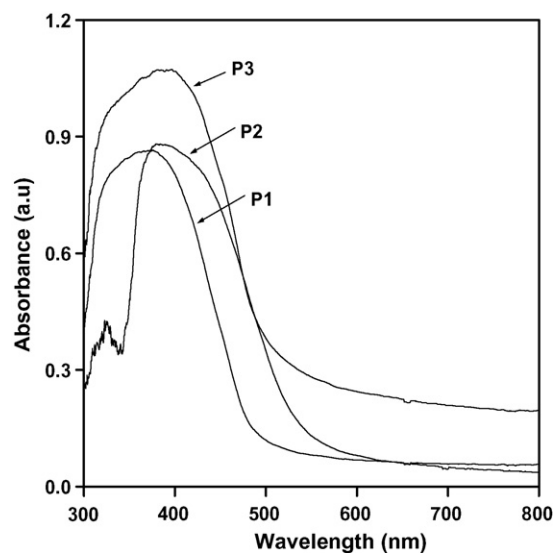


Fig. 2. UV–vis absorption spectra of the polymer thin films.

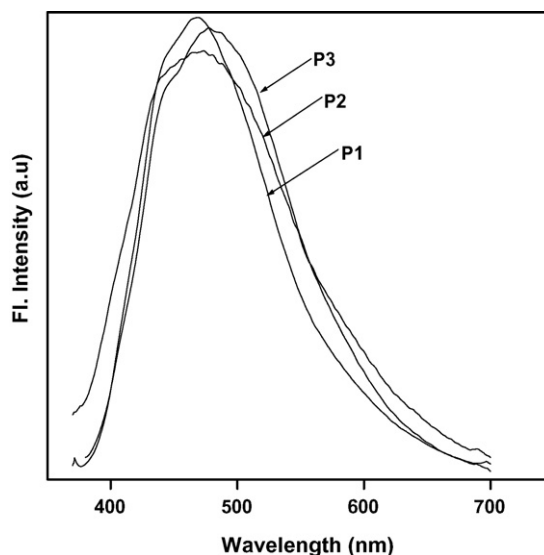


Fig. 3. Fluorescence emission spectra of P1–P3 in DMF solutions.

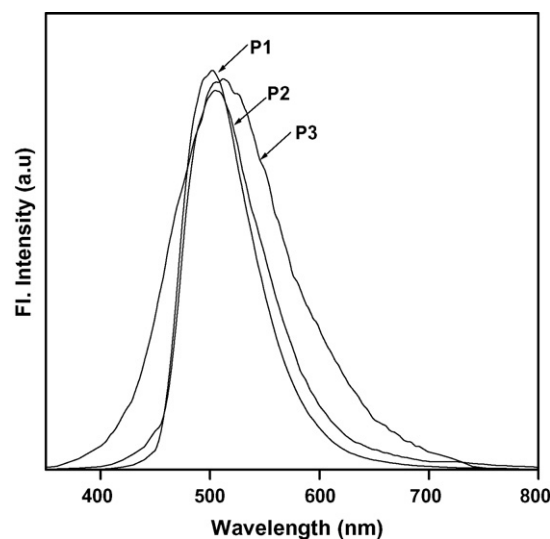


Fig. 4. Fluorescence emission spectra of the polymer thin films.

green light in solid state, with emission peaks at 502, 506 and 512 nm for **P1**, **P2** and **P3**, respectively. Consequently, the fluorescence spectra of the polymer thin films exhibit a red shift with respect to those obtained from their solutions. This can be attributed to the interchain or/and intrachain mobility of the excitons and excimers generated in the polymer in the solid stated phase. As depicted in Table 1, a sequential red shift in the  $\lambda_{\max}$  was observed in both the UV–vis absorption spectra and fluorescence emission spectra of polymers **P1–P3**. The increase in the length of the alkoxy side chains led to a red shift in the  $\lambda_{\max}$  in UV–vis absorption and fluorescence emission spectra. This can be interpreted as an expected better side chain interdigitation and interchain organization with increasing pendant chain length. The fluorescence quantum yields [30] of the polymers in solution were determined using quinine sulfate as a standard [31]. As shown in Table 1 the quantum yield of the polymers are in the range of 26–30%. These results indicate that the polymers can be used as light-emitting materials in devices.

Conjugated polymers are a promising class of third-order non-linear optical (NLO) materials because of their potentially large third-order susceptibilities associated with fast response time in addition to their variety and processability. Conjugated systems consisting of electron donor and electron acceptor units have showed enhanced third-order optical non-linearity [32]. Hence, we expected that polymers **P1–P3** with fully conjugated donor–acceptor arrangement might show good third-order non-linear optical properties. Preliminary studies on these polymers using Nd:YAG laser source yielded promising results and a detailed study is in progress.

### 3.3. Electrochemical properties

To study the electrochemical behavior, polymer thin films were coated on glassy carbon (GC) button electrode by evaporating the DMF solution of the polymers. The cyclic voltammetry (CV) was conducted in 0.1 M tetrabutylammoniumperchlorate solution in acetonitrile at a scan rate of 25 mV/s and the corresponding electrochemical data is summarized in Table 2. While sweeping cathodically, the polymers showed a reduction peak at around  $-1.4$  V (Fig. 5). These reduction potentials are lower than those of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) [17,33], one of the most widely used electron transporting materials, and are comparable with those of some good electron transporting materials [17]. In the anodic sweep, polymers showed an oxidation peak at around  $+1.25$  V suggesting that they can be used as hole transporting layer in LEDs [34]. However, we did not observe any linear dependence of redox potentials of these polymers on length of the alkoxy side chain

Table 2  
Electrochemical potentials and energy levels of the polymers

Polymer	$E$ (V) (oxd)	$E$ (V) (red)	HOMO (eV)	LUMO (eV)	$E_g$ (eV)
P1	1.25	-1.45	5.56	3.25	2.31
P2	1.20	-1.42	5.52	3.27	2.25
P3	1.23	-1.49	5.48	3.31	2.17

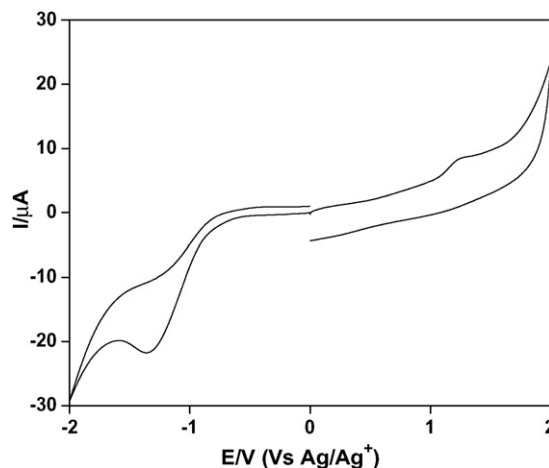


Fig. 5. Cyclic voltammogram of **P2** in 0.1 M TBAPC in acetonitrile at a scan rate of 25 mV/s.

at 3- and 4-positions of the thiophene ring. The onset potentials of n- and p-doping processes can be used to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of a conjugated polymer [35]. According to the equations reported by de Leeuw et al.,  $E_{\text{HOMO}} = [E_{(\text{onset})}^{\text{ox}} + 4.4 \text{ eV}]$  and  $E_{\text{LUMO}} = [E_{(\text{onset})}^{\text{red}} + 4.4 \text{ eV}]$ , where  $E_{(\text{onset})}^{\text{ox}}$  and  $E_{(\text{onset})}^{\text{red}}$  are the onset potentials versus SCE for the oxidation and reduction processes of a polymer, respectively. The HOMO energy levels of polymers **P1–P3** are estimated to be 5.56, 5.52 and 5.48 eV, respectively. These values are almost the same as that of poly(cyanoterphthalylidene) (CN-PPV), indicating that the polymers have similar hole-injection ability with CN-PPV when they are used in PLEDs. The LUMO energy levels of polymers **P1–P3** are estimated to be 3.25, 3.27 and 3.31 eV, respectively. These values are higher than those of CN-PPV, (3.02 eV) and some poly(aromatic oxadiazole)s (2.8–2.9 eV) [36], indicating that these polymers have better electron-injection ability when they are used in PLEDs. However, the LUMO energies of these polymers are comparable with those of some polyfluorene derivatives containing electron deficient 2-pyran-4-ylidene-malononitrile moiety [37]. The high electron affinities of polymers **P1–P3** may be attributed to the incorporation of electron deficient oxadiazole moiety and also the alternating p- and n-type arrangement along the polymers' backbone. A similar trend has been observed in some p-n diblock copolymers containing oxadiazole moiety [21]. From the onset potentials of oxidation and reduction processes, the band gaps of the polymers were estimated to be 2.31, 2.25 and 2.17 eV for polymer **P1**, **P2** and **P3**, respectively. The values are quite close to those obtained by the optical method.

## 4. Conclusions

A new series of polyoxadiazoles composed of 3,4-dialkoxythiophene and 1,4-divinylbenzene units have been synthesized using precursor polyhydrazide route. The polymers have well defined structure and displayed good thermal stability. All the polymers exhibited bluish-green fluorescence in

solutions and green fluorescence in thin films. The length of the electron-donating alkoxy chain at 3- and 4-positions of the thiophene ring influenced the optical properties of the polymers. Hence, a sequential red shift was observed in the  $\lambda_{\text{max}}$  of the UV–vis absorption spectra and the fluorescence emission spectra of the polymers **P1–P3**. Electrochemical studies reveal that the polymers possess low-lying LUMO energy levels (3.25–3.31 eV) and HOMO energy levels (5.48–5.56 eV) because of the alternate donor and acceptor conjugated units along the polymers' backbone, indicating that they may be promising candidates for electron transporting or hole blocking materials in light-emitting diodes. Further, these polymers are expected to show good third-order non-linear optical properties due to fully conjugated donor–acceptor arrangement along the polymers' backbone.

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