



Synthesis, characterization and optoelectrochemical properties of poly(1,6-bis(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexane) and its copolymer with EDOT

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ABSTRACT

A new polythiophene derivative was synthesized by electrochemical oxidative polymerization of 1,6-bis(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexane (TPH). The structure of the monomer was elucidated by ¹H, ¹³C, FTIR and mass analyses. The polymer P(TPH) and its copolymer with 3,4-ethylenedioxythiophene (P(TPH-co-EDOT)) were synthesized via potentiostatic electrochemical polymerization. Characterizations of the resulting polymers were performed by cyclic voltammetry (CV), FTIR, UV–vis spectroscopies and conductivity measurements. Moreover, the spectroelectrochemical and electrochromic properties of the polymer films were investigated. While P(TPH) has only three colors in oxidized and neutral states (blue, green and yellow), its copolymer with EDOT has five different colors (purple, red, light gray, green, and blue). Optical contrast and switching time of the polymer film were improved via copolymerization. It was found that with increasing applied potential the amount of PEDOT in the copolymer composition increases and band gap (E_g) of the copolymer decreases.

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1. Introduction

Conducting polymers (CPs) have recently received much attention in electrochromic applications [1–4]. CPs in particular have several advantages over inorganic compounds. These include outstanding coloration efficiency, fast switching ability [5], multiple colors with the same material [6] and fine-tuning of the bandgap (and the color) through chemical-structure modification [7]. For CPs, the electrochromism is related to doping–undoping process. The doping process modifies the polymer electronic structure, producing new electronic states in the band gap, causing color changes. Electronic absorption shifts bathochromically upon doping, and the color contrast between the undoped and doped states is related to the polymer band gap. A major focus in the study of electrochromic polymeric materials has been the control of colors via main-chain and pendant group structural modifications as well as copolymerization.

Among the electro-active organic polymers, polythiophene derivatives have occupied prime position due to its high conductivity, good redox reversibility, swift change of color with potential, and stability in environment [8]. Polythiophenes retain extensive

interest due to the technological applications such as non-linear optical devices [9], polymer light emitting diodes [10], gas sensors [11,12], organic transistors [13] and electrochromic devices [14,15].

Polythiophenes can be synthesized either chemically or electrochemically. Similar to polypyrrole, the mechanism of polymerization involves the formation of radical cations that react with each other to develop the polymeric structure. However, the potential required to oxidize the thiophene monomer also leads to overoxidation of the polymer itself. This is known as the “polythiophene paradox” [16]. In order to lower the potential, an approach that uses thiophene oligomers instead of thiophene monomer was suggested since oligomers can be polymerized at a considerably lower potential [17]. However, the resulting polymers exhibited even worse mechanical and electrical properties.

A special case of producing block copolymers is the chemical generation of dimers or trimers having two or more heteroaromatic rings derived from thiophene, furan and pyrrole [18,19]. In this way, we synthesized 1,6-bis(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexane (TPH) via Knorr–Paal reaction using 1,4-di(2-thienyl)-1,4-butanedione and hexane-1,6-diamine [20,21]. This route is convenient for the preparation of “trimeric” thiophene–pyrrole–thiophene derivatives substituted at the N atom of pyrrole ring. This strategy yields centrosymmetric polymer precursors and seeks to minimize the steric influence of the central substituent through

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the addition of the thiophene spacers. Thus, thiophene paradox is overcome and chemical and electrochemical polymerization of (TPH) can easily be achieved. The resultant products were characterized via several techniques such as cyclic CV, ^{13}C and ^1H NMR, FTIR, mass analyses and conductivity measurements. Electrochromic and spectroelectrochemical behaviors of the polymer were also studied.

Specific monomers, containing the desired functionalities are required for copolymer synthesis. Copolymerization can lead to an interesting combination of the properties. For that matter, we also synthesized a novel copolymer of TPH with 3,4-ethylenedioxythiophene (EDOT). EDOT is a popular choice as a comonomer since it produces a low band gap polymer with high stability and good conductivity [22]. EDOT and its derivatives can give rise to non-covalent intramolecular interactions with adjacent thiophenic units and thus, induce self-rigidification of the conjugated system in which it is incorporated [23,24]. The resultant copolymer was characterized via cyclic voltammetry, FTIR and conductivity measurements. The optoelectrochemical and electrochromic properties, such as the relative luminance, change of color upon redox switching, and switching stability of the copolymer were determined. While P(TPH) has only three colors in oxidized and neutral states (blue, green and yellow), its copolymer with EDOT has five different colors (purple, red, light gray, green, and blue). Optical contrast and switching time of the polymer film were also enhanced with copolymerization.

2. Experimental

2.1. Materials

AlCl_3 (Aldrich), succinyl chloride (Aldrich), dichloromethane DCM (Merck), *p*-toluene-sulfonic acid (PTSA) (Aldrich), hexane-1,6-diamine (Aldrich), toluene (Sigma), acetonitrile AN (Merck), EDOT (Aldrich), LiClO_4 (Aldrich), thiophene (Aldrich), NaHCO_3 (Aldrich), MgSO_4 (Aldrich) were used without further purification.

2.2. Equipments

A three-electrode cell containing an ITO-coated glass slide as the working electrode, a platinum foil as the counter electrode, and a silver wire as the pseudo reference electrode were used for electrodeposition of polymer films via potentiostatic or potentiodynamic methods. N_2 gas was passed through the solution to provide an inert atmosphere. All electrochemistry experiments were carried out using a Voltalab PST 50 model potentiostat/galvanostat. NMR spectra were recorded on a Bruker-Instrument NMR Spectrometer DPX-400 by using CDCl_3 as the solvent. The FTIR spectrum was recorded on a Nicolet 510 FTIR spectrometer. Mass spectrum was recorded in a Waters Micromass Quatro MicroGC operating at 20 eV using direct insertion probe. Melting points

were determined in open capillary tubes in a Schorpp Geratetechnik SMPH melting point apparatus. Electrical conductivity of the polymers was measured at room temperature by using four probe technique with a home made instrument. Spectroelectrochemical studies were carried on Agilent 8453 UV-vis spectrophotometer. Colorimetry measurements were done via Minolta CS-100 spectrophotometer.

2.3. Synthesis of 1,6-bis(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexane (TPH)

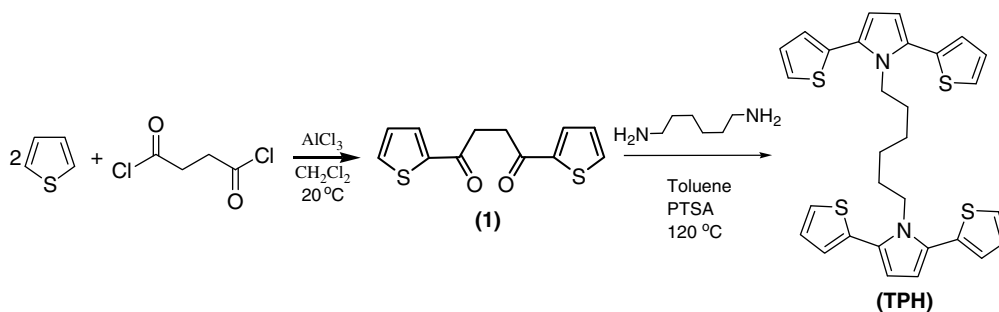
The starting material, 1,4-di(2-thienyl)-1,4-butanedione (**1**), was synthesized according to literature procedure [14]. To a suspension of 0.12 mol AlCl_3 in 15 ml CH_2Cl_2 , a solution of thiophene (0.12 mol) and succinyl chloride (0.05 mol) in CH_2Cl_2 were dropwise added. The mixture was stirred at room temperature for 4 h. This was then poured into ice and concentrated HCl (5 ml) mixture. The dark green organic phase was washed with concentrated NaHCO_3 (3×25) ml and brine, and then dried over MgSO_4 . After evaporation of the solvent a blue-green solid suspended in ethanol. Filtration and washing with ethanol yielded 1,4-bis-2-thienylbutane-1,4-dione. The monomer (TPH) was synthesized from 1,4-di(2-thienyl)-1,4-butanedione and hexane-1,6-diamine in the presence of catalytical amount of *p*-toluenesulphonic acid (PTSA). A round-bottomed flask equipped with an argon inlet and magnetic stirrer was charged with 15 mmol 1,4-di(2-thienyl)-1,4-butanedione, 7 mmol hexane-1,6-diamine, 1.2 mmol PTSA and 20 ml toluene. The resultant mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene followed by flash column chromatography SiO_2 column, and elution with dichloromethane afforded the desired compound as a pale yellow powder (mp 142–143 °C) [20]. The synthetic route of the monomer is shown in Scheme 1.

2.4. Cyclic voltammetry

The oxidation/reduction behavior of TPH (0.01 M) was investigated by CV in 0.1 M LiClO_4/AN . Experiments were carried out in an electrolysis cell equipped with indium/tin oxide (ITO) coated glass plate as the working, Pt wire as the counter and Ag wire as the pseudo reference electrodes. The measurements were carried out at room temperature under nitrogen atmosphere. In order to investigate the electrochemical behavior of the copolymer, CV studies were performed in the presence of TPH (0.01 M) and EDOT (0.01 M) under same experimental conditions.

2.5. Electrochemical homopolymerization and copolymerization of TPH

TPH (0.01 M) was dissolved in 15 mL AN and 0.1 M LiClO_4 were introduced into a single compartment electrolysis cell. Electrolysis



Scheme 1. Synthetic route for the monomer.

was run for 10 min at 1.1 V at room temperature under inert atmosphere. For electrochemical synthesis of copolymer, TPH (0.01 M), EDOT (0.01 M) and LiClO_4 (0.1 M) were dissolved in AN and electrolysis was run for 5 min at 1.2 V. Resulting homopolymer and copolymer films were washed with AN to remove LiClO_4 after the electrolysis.

3. Results and discussion

3.1. ^1H NMR and ^{13}C NMR spectra

The structure of the monomer was confirmed by ^1H NMR and ^{13}C NMR spectral analyses. The ^1H NMR and ^{13}C NMR spectra of the monomer have the characteristic peaks of the structure (see Supplementary material).

^1H NMR (400 MHz, 25 °C, in CDCl_3) δ = 7.3 (d; 4H), 6.95 (dd; 4H), 6.9 (dd; 4H), 6.25 (s; 4H), 3.95 (t; 4H), 1.35 (m; 4H), 0.85 (m; 4H).

^{13}C NMR (400 MHz, 25 °C, in CDCl_3) δ = 135.0, 128.3, 127.3, 126.0, 125.3, 110.8, 44.9, 31.0, 25.8. MS: m/e 544 (M^+).

3.2. FTIR spectrum

The IR spectral characteristics of the monomer are discussed together with the electrochemically prepared polymers. FTIR spectrum of the TPH shows the following absorption peaks: 3100–3070 cm^{-1} C–H stretching vibration (pyrrole and thiophene), 2924 cm^{-1} and 2855 cm^{-1} correspond to aliphatic methylene stretching, 1620 cm^{-1} C=C stretching vibration, 1494 and 1340 cm^{-1} aromatic C=C, C–N stretchings due to pyrrole, 1033 cm^{-1} C–H deformation vibration for 1-subst. pyrrole, 756 cm^{-1} C–H deformation vibration of 1,2,5-trisubstituted pyrrole, 686 cm^{-1} C–H out-of-plane deformation vibration of thiophene.

Most of the characteristic peaks of the monomer remained unperturbed upon electrochemical polymerization. The broad band observed at around 1649 cm^{-1} proves the presence of polyconjugation and new peaks at 1113, 1087 and 620 cm^{-1} were attributed to the incorporation ClO_4^- ions into the polymer film during doping process.

After the electrochemical copolymerization of TPH with EDOT, the disappearance of peaks at 773 and 3100 cm^{-1} are evidences of the polymerization through 2, 5 positions of thiophene ring.

The shoulder observed at 1645 cm^{-1} is due to the conjugation and peaks at 1144 cm^{-1} due to C–O–C group indicates that EDOT is incorporated to the polymer matrix. The peaks appeared at 1089, 1113 and 632 cm^{-1} show the presence of the dopant ion, ClO_4^- .

3.3. Cyclic voltammetry

When redox behavior of TPH was investigated via cyclic voltammetry, an electrochromism between yellow and blue colors was observed, while a greenish cloud was formed around the electrode due to the partial dissolution of linear oligomers. Cyclic voltammogram of TPH in AN showed two oxidation peaks at +0.63 and +1.1 V and a reduction peak at +0.47 V. After subsequent runs electroactivity increases with increasing scan number. The peak at +1.1 V decreases as a result of monomer consumption in the diffusion layer (Fig. 1a).

To investigate the copolymer we performed CV studies in the presence of EDOT under 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 than those of TPH and EDOT, which in fact, could be interpreted as the formation of copolymer (Fig. 1).

3.4. Scan rate dependence of the peak currents

P(TPH) and P(TPH-co-EDOT) films were prepared via constant potential electrolysis. Their redox switching in monomer free electrolyte revealed a single, well-defined redox process. Figs. 2 and 3 show cyclic voltammograms of P(TPH) and P(TPH-co-EDOT) at different scan rates. The current responses were directly proportional to the scan rate indicating that the polymer films were electroactive and well adhered to the electrode [15]. The scan rates for the anodic and cathodic peak currents show a linear dependence as a function of the scan rate as illustrated in inserted figures in Figs. 2 and 3 for P(TPH) and P(TPH-co-EDOT), respectively. This demonstrates that the electrochemical processes are not diffusion limited and reversible even at very high scan rates.

3.5. Conductivities of the films

The conductivities of the films were measured via four probe technique. The conductivity of electrochemically prepared homo-

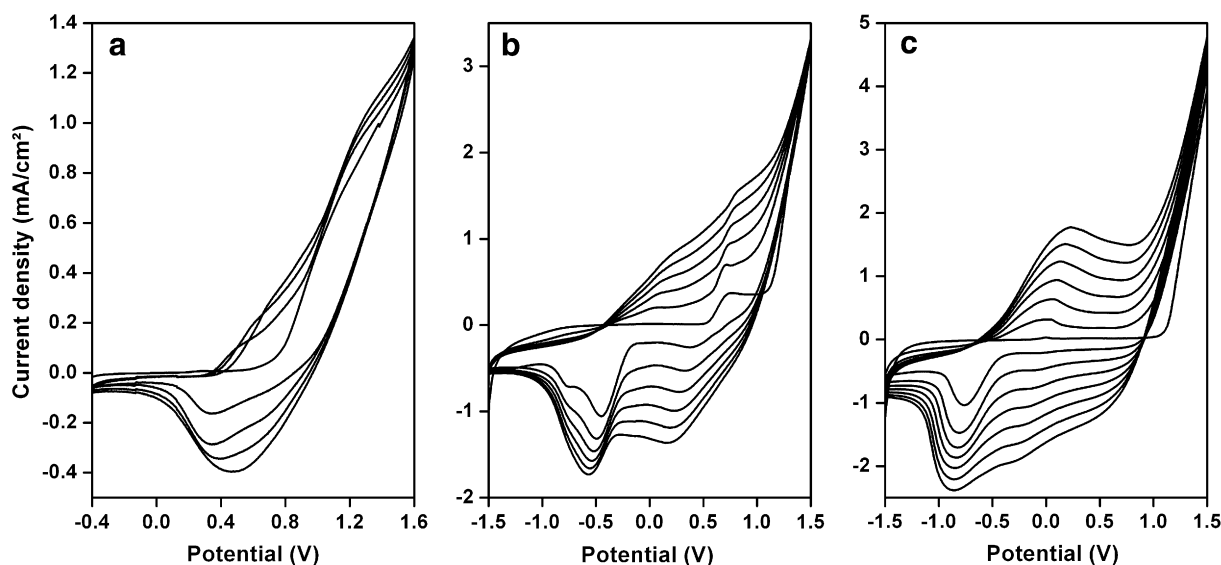


Fig. 1. Cyclic voltammograms of (a) TPH, (b) TPH in the presence of EDOT, (c) EDOT, on ITO glass electrode in 0.1 M LiClO_4/AN at 250 mV/s scan rate.

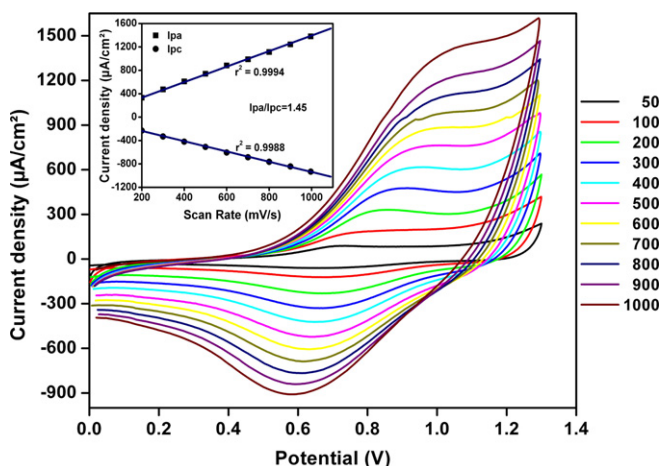


Fig. 2. Cyclic voltammograms of P(TPH) at different scan rates. Inset figure shows peak current vs scan rate graph.

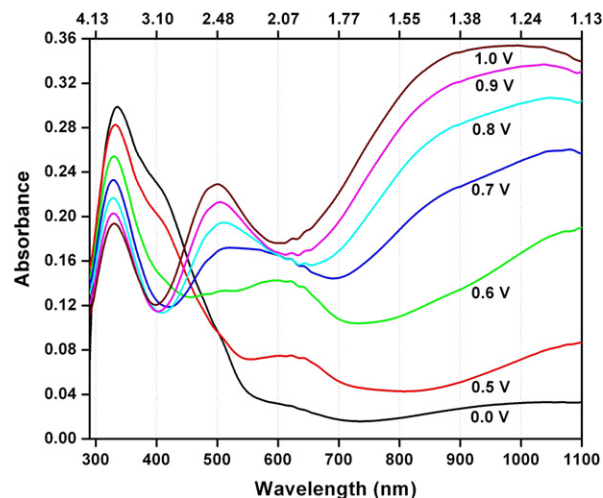


Fig. 4. Optoelectrochemical spectra of P(TPH) film at applied potentials between 0.0 and +1.0 V.

and electrochromic properties of the resultant copolymer were studied by applying potentials between -0.2 and $+1.1$ V in a monomer free ACN/LiClO₄ (0.1 M) medium. At the neutral state λ_{max} value due to the π - π^* transition of the copolymer was found to be 454 nm and E_g was calculated as 1.89 eV (Fig. 5).

3.7. Colorimetry

The color of an electrochromic material was defined accurately by performing colorimetry measurements. The Commission Internationale de l'Eclairage (CIE) system was employed as the quantitative scale to define and compare colors. Colorimetry measurements were performed in the same electrolyte using the Minolta CS-100 Spectrophotometer. Three features of color; hue (a), saturation (b) and luminance (L) were measured and recorded in Table 1. The P(TPH) film shows different colors in the fully reduced (0.0 V) and oxidized states (+1.0 V). The color of the film switches from a blue color in the oxidized form to yellow in the reduced state. The copolymer P(TPH-co-EDOT) reveals multichromic property with five different colors with applied potentials between -0.2 and $+1.1$ V.

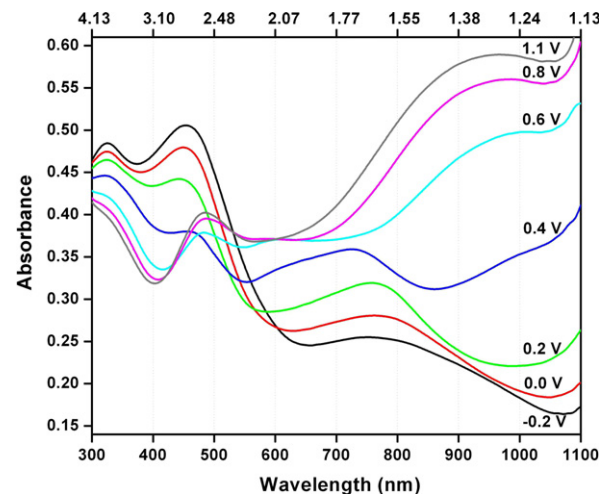


Fig. 5. Optoelectrochemical spectra of P(TPH-co-EDOT) film at applied potentials between -0.2 and $+1.1$ V.

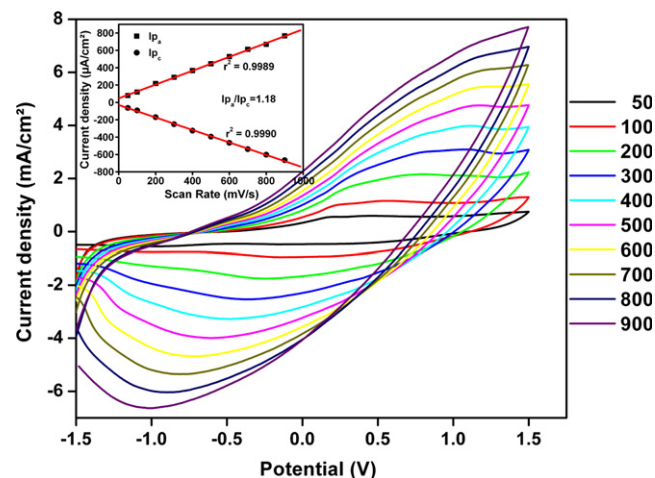


Fig. 3. Cyclic voltammograms of P(TPH-co-EDOT) at different scan rates. Inset figure shows peak current vs scan rate graph.

polymer was $3.0 \times 10^{-5} \text{ S cm}^{-1}$; whereas P(TPH-co-EDOT) was measured as $5 \times 10^{-2} \text{ S cm}^{-1}$. Introducing EDOT into the polymer chain increased the conductivity.

3.6. Electrochromic properties of polymers

The best way of examining the changes in optical properties of conducting polymers upon voltage change is via spectroelectrochemistry. It also gives information about the electronic structure of the polymer such as band gap (E_g) and the intergap states that appear upon doping.

P(TPH) film was electrochemically synthesized on an ITO electrode in AN/LiClO₄ solvent/electrolyte couple. The spectroelectrochemistry studies of the P(TPH) were studied by applying potentials between 0.0 and 1.0 V in a monomer free AN/LiClO₄ (0.1 M) medium. The wavelength (λ_{max}) at which polymer shows π - π^* transition was determined as 335 nm. The band gap (E_g) was calculated as 2.16 eV (Fig. 4).

P(TPH-co-EDOT) was potentiostatically synthesized at 1.2 V on ITO electrode. Electrolyte solution was composed of 0.01 M TPH, 0.01 M EDOT and ACN/LiClO₄ (0.1 M). The spectroelectrochemical

Table 1
Electronic and electrochromic properties of the polymers

Polymer	λ_{\max} (nm)	Potential (V)	L	a	b	Color	E_g (eV)
P(TPH)	335	0.0	80	-4	62	Yellow	2.16
		+0.4	53	-12	9	Green	
		+1.0	39	-3	-18	Blue	
P(TPH-co-EDOT)	454	-0.2	52	20	1	Purple	1.89
		+0.0	62	16	10	Brown	
		+0.2	75	-3	11	Green	
		+0.4	78	-15	-4	Teal	
		+1.1	75	-10	-13	Blue	
PEDOT	600	+1.3	91	-8	-11	Light blue	1.60
		-1.0	40	-15	-35	Blue	

3.8. Switching

The ability of a polymer to switch without delay and exhibit a sharp color change are very significant. Double potential step chronoamperometry was carried out to estimate the response time of the device. The potential was stepped between fully oxidized and neutral states of the polymer film with a residence time of 5 s.

During the experiment, the percent transmittance ($T\%$) at the wavelength of maximum contrast was measured using a UV–vis spectrophotometer.

For P(TPH) maximum contrast ($\Delta T\%$) and switching time were measured as 28% and 1.2 s, respectively, by stepping the potential between 0.0 and +1.1 V with a residence time of 5 s. Switching time and $\Delta T\%$ values for P(TPH-co-EDOT) were measured as 0.8 s and 32% respectively while stepping the potential between -0.2 and +1.1V (see Supplementary material).

3.9. In situ electrochemical copolymerization

In situ electrochemical copolymerization of TPH and EDOT was carried out in a solution containing 0.01 M TPH and 0.01 M EDOT in LiClO_4 (0.1 M)/ACN solvent–electrolyte couple by applying different potentials. During the electrolysis, UV–vis spectra were taken for every 10 s time interval. Fig. 6a–d shows in situ electrochemical copolymerization of TPH and EDOT.

It was found that absorbance changes recorded with the square root of the time at different wavelengths changes linear. Linearity between absorbance and square root of the time proves that polymerization rate is controlled by diffusion (see Supplementary material).

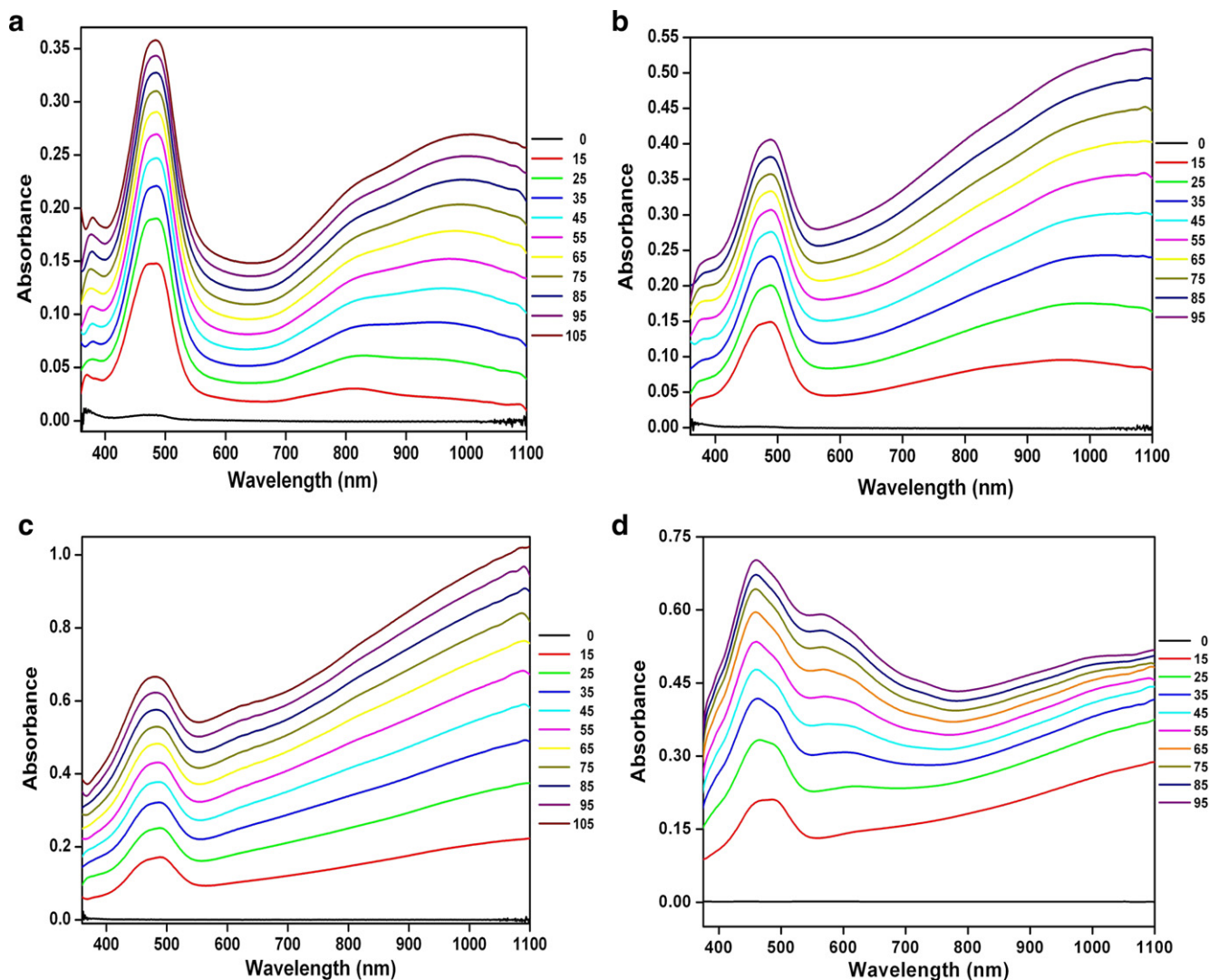


Fig. 6. In situ electrochemical copolymerization of TPH and EDOT with different applied potentials (a) 1.1 V, (b) 1.2 V, (c) 1.3 V, (d) 1.5 V.

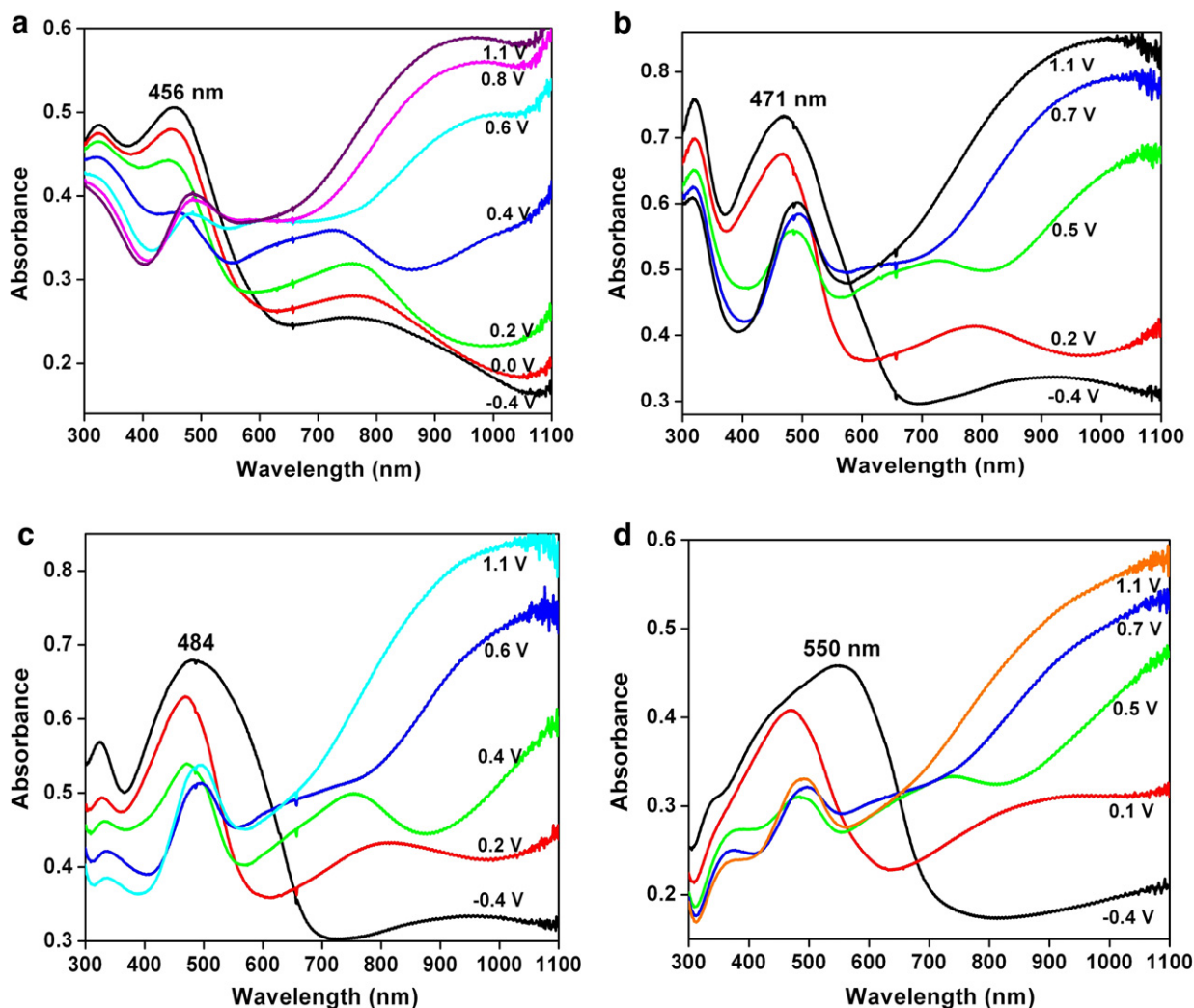


Fig. 7. Optoelectrochemical spectra of copolymers synthesized at different potentials (a) 1.1 V, (b) 1.2 V (c) 1.3 V and (d) 1.5 V.

3.10. Spectroelectrochemical studies of copolymers obtained by different applied potentials

In order to investigate spectral properties of the copolymers spectroelectrochemistry studies were performed. Polymers were obtained by constant potential polymerization in the presence of AN/LiClO₄ solvent–electrolyte couple by varying the potential between 1.1 and 1.5 V. Knowing that the λ_{\max} of the homopolymer is 335 nm and that of the PEDOT is 600 nm, maximum absorption wavelength values were obtained in this range. It should be noted that as the amount of PEDOT in the copolymer composition increases by increasing the potential, band gap (E_g) of the copolymer decreases and λ_{\max} of the copolymer shifts closer to 600 nm (Fig. 7).

Table 2
 λ_{\max} and E_g values of copolymers prepared with different applied potentials

Polymers	Potential (V)	λ_{\max} (nm)	E_g (eV)
P(TPH)	1.1	335	2.16
COP1	1.1	456	1.84
COP2	1.2	471	1.81
COP3	1.3	484	1.74
COP4	1.5	550	1.67
PEDOT	1.3	600	1.60

Table 2 summarizes a comparison among homopolymer, PEDOT and copolymers prepared via applying different potentials. Maximum wavelengths of the copolymers are between those of PEDOT and homopolymer. As seen from Table 2, introduction of EDOT to the polymer chain led to a tremendous decrease in the band gap. These numerical values also support the realization of copolymerization.

4. Conclusion

A new thiophene derivative, 1,6-bis(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexane (TPH), was successfully synthesized. The structure of the monomer was elucidated by ¹H and FTIR. P(TPH) and its copolymer with 3,4-ethylene dioxythiophene (P(TPH-co-EDOT)) were synthesized via potentiostatic electrochemical polymerization. Characterizations of the resulting polymers were performed by CV, FTIR, UV–vis spectroscopy and conductivity measurements.

Spectroelectrochemical studies and electrochromic characterization methods showed that copolymerization with EDOT not only decreases the band gap (E_g) but also enhances the electrochromic properties such as optical contrast and switching time. It was also found that as the amount of PEDOT in the copolymer composition increases, band gap (E_g) for the copolymer decreases and λ_{\max} value of the copolymer shifts to 600 nm (λ_{\max} for PEDOT).

Scan rate dependence of the peak currents measurements show that the current responses were directly proportional to the scan rate indicating that the electrochemical processes are not diffusion limited and reversible even at very high scan rates and the polymer films were electro-active and adhered well to the electrode.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jelechem.2008.04.015](https://doi.org/10.1016/j.jelechem.2008.04.015).

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