Journal of Macromolecular Science, Part A

Pure and Applied Chemistry

ISSN: 1060-1325 (Print) 1520-5738 (Online) Journal homepage: https://www.tandfonline.com/loi/lmsa20

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To cite this article: Hüseyin Kalay, Deniz Yiğit, Gonul Hizalan, Mustafa Güllü, Tolga Depci, Ali Cirpan, Levent Toppare & Serife O. Hacioglu (2020) Synthesis, electrochromic characterization and solar cell application of thiophene bearing alternating copolymers with azobenzene and coumarin subunits, Journal of Macromolecular Science, Part A, 57:8, 589-599, DOI: 10.1080/10601325.2020.1740598

To link to this article: https://doi.org/10.1080/10601325.2020.1740598

JOURNAL OF MACROMOLECULAR SCIENCE, PART A: PURE AND APPLIED CHEMISTRY
2020, VOL. 57, NO. 8, 589–599
https://doi.org/10.1080/10601325.2020.1740598

Synthesis, electrochromic characterization and solar cell application of thiophene bearing alternating copolymers with azobenzene and coumarin subunits

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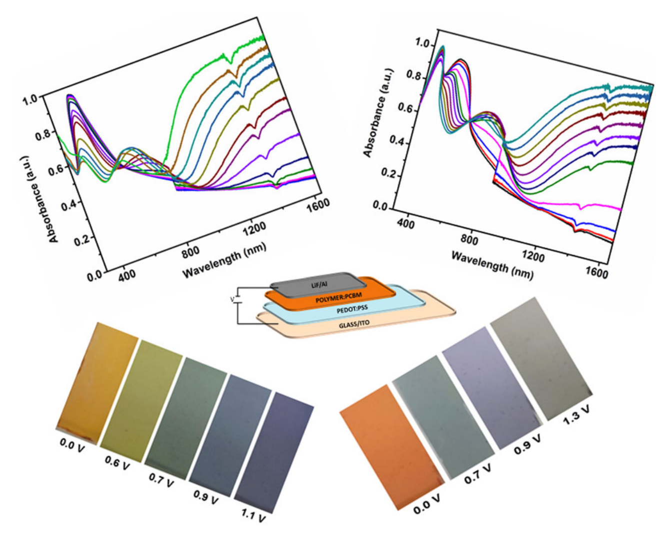
ABSTRACT

In this study, azobenzene and coumarin functionalized thiophene comprising two copolymers (poly (4-((3‴-hexyl-[2,2′:5′,2″:5″,2‴-tetrathiophene] − 3′-yl)methoxy) - 2H-chromen-2-one (P1) and poly (1-(4-((4‴-hexyl-[2,2′: 5′, 2″: 5″, 2‴ - tetrathiophene] − 3′-yl) methoxy) phenyl) −2-phenyldiazene) (P2)), were designed and synthesized according to the donor–acceptor (D–A) approach to investigate their electrochemical, optical and photovoltaic behaviors. Among the various copolymerization methods to obtain P1 and P2, Stille copolymerization reaction was preferred. The HOMO and LUMO values were determined via cyclic voltammetry (CV) as −5.64 eV and −3.76 eV for P1 and −5.47 eV and −3.83 eV for P2, respectively. The optical band gaps of the polymers were calculated as 1.88 eV and 1.64 eV using UV-VIS spectrophotometer for P1 and P2. Electrochemical and spectroelectrochemical studies for synthesized copolymers support their usage in organic solar cell applications. The organic solar cells (OSCs) were designed using polymer as an electron donor group and PC$_{60}$BM as an electron acceptor group. Performances of OSCs based on P1 and P2 were investigated with the device structure of ITO/PEDOT:PSS/Polymer(P1/P2):PC$_{60}$BM/LiF/Al. The preliminary solar cell results were reported here and studies are going on in our laboratories to increase the efficiency. The highest power conversion efficiency was obtained as 0.81% for P1 based device with 0.47 V open-circuit voltage (V$_{oc}$) and 4.92 mA/cm^2 current density (J$_{sc}$) values. The highest efficiency for P2 comprising device was found to be 0.96% under optimum conditions with 0.60 V and 4.98 mA/cm^2, V$_{oc}$ and J$_{sc}$ values, respectively.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received February 2020
Accepted March 2020

KEYWORDS
Azobenzene; solar cell; thiophene bearing copolymers; coumarin; conducting polymers

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1. Introduction

In order to meet the increasing energy demand, fossil fuel consumption is also increasing accordingly. However, because of the limited amount of fossil fuels available, there is a worldwide energy crisis. In addition, increasing amounts of fossil fuels to meet energy demands emit carbondioxide and cause global warming. Therefore, the demand for renewable energies which are alternative sources for fossil fuels is increasing around the world. Renewable energy is derived from natural resources which can be listed as solar energy, wind energy, wave energy, geothermal energy, hydraulic energy and biomass energy. 20.0% of the total electrical energy demand in the Europe will be met by renewable energy sources (RES) in 2020.[1] Also in the world, solar energy is one of the most popular renewable energy sources with the greatest amount of studies in the field and major developments in a short time. This energy source is cheap and environmentally friendly, and has been the subject of many experimental studies. In addition, solar energy can be integrated with different systems so that it takes a big part in energy saving policy. Most of the materials used for photovoltaics are inorganic materials, however in recent years many studies have been performed to develop organic solar cells.[2] Compare to inorganic solar cells, organic solar cells have some certain advantages such as; large area applicability, easy structural modification, light weight, low cost and easy manufacture.[3,4] There are many studies in literature for usage of conjugated polymers in the construction of organic solar cells. Conjugated polymers have some advantageous namely low cost, easy preparation, high solubility, easy modification and can be used with flexible surfaces. Due to these advantages, they can be used in many fields of applications such as; organic solar cells, thin film transistors, electrochromic materials and sensors.[5–8] One of the most useful strategy for the conjugated polymer design is the combination of electron donor and acceptor groups in the polymer backbone. These functional groups have an important role in determining the optical and electronic properties of the resulting polymers. These properties vary not only with these groups but also with the modification of π bonds in the structure. In literature, there are a number of examples for such polymers synthesized via donor acceptor approach.[9,10] While benzotriazole, quinoxaline, bezothiadizole and tetrachlorethylene are widely used as electron acceptor materials, thiophene, 3-hexylthiophene, 3,4-ethylenedioxythiophene (EDOT) and carbazole are widely preferred as electron donor materials. Polythiophene is a conjugated polymer that becomes electronically conductive via doping process, however unfortunately, this polymer is insoluble in common organic solvents. The addition of alkyl groups to the third position of this polymer improve the solubility and processability of the polymer in many organic solvents.[11] Among the large number of conductive polymers, polythiophene has been widely used for many years due to its potential applications in organic electronics, drug design, electronic devices, biodiagnostics and sensory devices due to high environmental stability property.[12,13] Like most conducting polymers, polythiophene derivatives are electrochromic materials which permanently change their colors reversibly upon applied potential.[14] Compared to other conjugated polymers, functionalization and changing substituents of polythiophenes are relatively easy and polythiophene derivatives have many advantages such as, chemical stability, ease of synthesis and modification, low band gap, high stability in oxidized forms, good electrical conductivity.[15,16] In literature, there are lots of studies in which azobenzene is used as a substituent for polythiophenes. Azobenzene is an aryl azo compound consisting of two phenyl rings linked together by an N=N bond. The azobenzene groups in three positions will not only satisfy better processability and stability, but also result in improved electrical, electrochemical and optical properties.[17,18] Another type of substituent for copolymer is coumarin unit which is a benzopyrone class. Coumarins have various biological properties such as antimicrobial, antiviral, antioxidant and enzyme inhibiting. Furthermore, coumarin comprising polymers have important industrial applications such as organic-inorganic hybrid materials, liquid crystal materials, light storage/energy transfer materials due to its structural properties.[19] Electrochromism is another important property for conducting polymers which relates to the changing color of polymers via doping-dedoping processes. Since the difference between the HOMO and LUMO energy levels is in the visible region of the electromagnetic spectrum for conductive polymers, they are often colored in their neutral state.[20,21] During the doping process, new low-energy transitions occur in the band gap (Eg) causing color changes in the polymer.

In literature thiophene comprising conducting polymers were widely used for electrochromic and organic solar cell applications.[22–24] Qunping Fan et al. synthesized fluorine substituted polythiophene in their study and used for photovoltaic applications. The fluorine substituent gave the polymer a deeper HOMO energy level with a lower band gap and a high crystallinity. The resulting polymer and PCBM based organic solar cells yielded a PCE of 9.2% which is one of the highest values reported for the PT derivatives-based PSCs.[22] Özge Azeri et al. synthesized copolymers containing benzodithiophene and thienopyrroledione in their study and examined the applications of these copolymers in organic solar cells. The best performance deviced with these copolymers was observed for P2 with 5.83% power conversion efficiency with 0.80 V Voc and 14.02 mA/cm^2 Isc values.[23]

In the light of these knowledge, azobenzene and coumarin functionalized thiophene comprising copolymers (P1 and P2) were designed and synthesized with thiophene bridge via chemical polymerization techniques for electrochromic and organic solar cell applications in this study. Electrochemical, electrochromic and spectroelectrochemical analysis of the resulting copolymers were carried with cyclic voltammetry (CV) and UV-Vis spectrophotometer techniques. Both copolymers exhibited multichromic behavior with orange neutral state colors and 1.88 eV/1.64 eV optical band gaps, respectively. Finally both P1 and P2 were used as the donor materials and mixed with PCBM in the active layer of organic solar cells. The highest efficiency for P2 based OSC was found to be 0.96% under optimum annealing conditions with 0.60 V, Voc and 4.98 mA/cm^2, Jsc values.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Sigma- Aldrich Chemical Co. Ltd. and used without any further purification. Polymers were dissolved in $CHCl_3$(5 mg mL^{-1}) and spray processed on an ITO coated glass substrate for electrochemical, spectroelectrochemical and kinetic studies. Cyclic voltammetry studies were conducted via Gamry Reference 600 potentiostat/galvanostat in a three-electrode cell (ITO coated glass slide, Pt wire and Ag wire as the working electrode, the counter electrode and reference electrode). JASCO V-770 spectrophotometer integrated with potentiostat was used for optical and spectroelectrochemical studies. For OSC characterizations, the current density-voltage (J-V) characteristicswere determined with a Keithley 2400 source measurement unit under AM 1.5 solar simulator.

2.2. Synthesis of polymers

2.2.1. Synthesis of 3- (bromomethyl) thiophene(3)

3-Methylthiophene (5.5 g, 5.6 mmol) was placed in a single neck flask and dissolved completely in 15 mL of CCl_4. NBS (8.5 g, 5 mmol) and the radical initiator reagent benzoyl peroxide (0.02 g, 0.082 mmol) were added to the carbon tetrachloride solution and boiled under reflux. After about 20 minutes, more benzoyl peroxide (0.02 g, 0.082 mmol) was added to the reaction medium and the reaction was continued for 6 hours. At the end of the reaction, the solution was cooled to room temperature and the succinimide residues were filtered off from the carbon tetrachloride phase. CCl_4 was recovered by ordinary distillation. The resulting oily product was purified by distillation under reduced pressure with 74% yield.

^{1}H NMR spectrum ($CDCl_3$) δ/ppm: 4.5 (t, 2H), 7.06 (s, 1H), 7.2 (s, 1H), 7.3 (s, 1H).

2.2.2. The general synthesis method of thiophene derivatives containing azobenzene, coumarin(1-Phenyl-2-(4- (thiophen-3-ylmethoxy) phenyl)(4)diazene and 4-(thiophen-3-ylmethoxy)-2H-chromen-2-one))(5)

Thiophene derivatives containing strong chromophore groups such as azobenzene, coumarin and fluorescein were generally synthesized by synthesis method based on nucleophilic substitution reactions. Firstly, the test apparatus was slowly heated with burner under nitrogen atmosphere to remove any possible moisture. Then, 3- (bromomethyl) thiophene (7.34 mmol) and chromophore compound (7.34 mmol) were placed in the reaction flask and dissolved completely in 50 mL of freshly prepared dry DMF. Cesium carbonate (Cs_2CO_3) (29.36 mmol) was added to the DMF solution, followed by vigorous stirring at room temperature for 15 minutes. The reaction was then continued for 24 hours under reflux and nitrogen atmosphere at 120° C. At the end of the reaction, the DMF content was cooled to room temperature and poured into 100 mL of ice water and taken to pH = 11-12. The solid product which precipitated in the aqueous phase was dried under vacuum and purified using the appropriate purification technique. Structural analyzes of target products were performed using ^{1}H NMR and FTIR techniques.

2.2.2.1. 1-Phenyl-2-(4-(thiophen-3-ylmethoxy) phenyl) diazene (4). It was synthesized by nucleophilic substitution reaction of 3- (bromomethyl) thiophene and p-hydroxyazobenzene according to general synthesis methods. The crude product was purified by column chromatography using hexane.

FTIR spectrum (ATR) vmax/cm^{-1}: 3098 (thiophene aromatic CH stretch), 3068 (benzene aromatic CH stretch), 2948-2908 (aliphatic C-H stretch), 1600, 1581 (aromatic) C=C stretch), 1494-1413 (aliphatic CH stretch), 1236 (CO stretch).

1 H NMR spectrum ($CDCl_3$) δ/ppm: 5.166 (t, 2H), 7.08 (d, *J=9.2* Hz, 2H, He), 7.18 (m, 1H) , 7.37 (m, 2H), 7.46 (m, 3H), 7.9 (m, 4H).

2.2.2.2. 4-(Thiophen-3-ylmethoxy)-2H-chromen-2-one (5). 3-(Bromomethyl) thiophene and 4-hydroxycoumarin were mixed to synthesize 4-(thiophen-3-ylmethoxy)-2H-chromen-2-one by nucleophilic substitution reaction according to general synthesis methods. The crude product was purified by crystallization from ethanol/water (1: 1).

FTIR spectrum (ATR) vmax/cm^{-1}: 3103 (thiophene aromatic CH stretch), 3082 (benzene aromatic CH stretch), 2972-2933 (aliphatic C-H stretch), 1708, 1690 (C=O stretch), 1624-1566 (aromatic C=C stretch), 1492-1333 (aliphatic CH stretch), 1247 (CO stretch).

^{1}H NMR spectrum ($CDCl_3$) δ/ppm: 5.22 (t, 2H), 5.78 (t, 1H), 7.19 (m, 1H), 7.24 – 7.28 (m, 1H), 7.32-7.34 (d, $J = 7.6$ Hz), 7.41 (m, 2H), 7.55 (m, 1H), 7.88 (d, $J = 8$ Hz and $J = 1.6$ Hz).

2.2.3. The general synthesis method of dibromothiophene derivatives containing chromophore group (1- [4 -((2,5-Dibromthiophen-3-ylmethoxy) phenyl] -2-phenyldiazene (6) and 4 - [(2,5-Dibromthiophen-3-ylmethoxy)]- 2H-chromen-2-one (7))

Firstly, the reaction flask and all other glassware were completely covered with aluminum foil to isolate the test apparatus from daylight. The thiophene derivatives (2 and 3) (2.8 mmol) were then added to the reaction flask, dissolved in 20 mL of dry DMF and cooled to 0° C in an ice bath. Then, a solution of NBS (1 g, 5.62 mmol) in 15 mL of DMF was slowly added to the reaction medium over a period of 1 hour using a dropping funnel. After stirring for 24 hours at room temperature, the DMF content was poured into 100 mL of ice-water. The aqueous phase was extracted with $CHCl_3$ (3×50 mL) then dried over Na_2SO_4. After the organic solvent was recovered from the rotary evaporator,

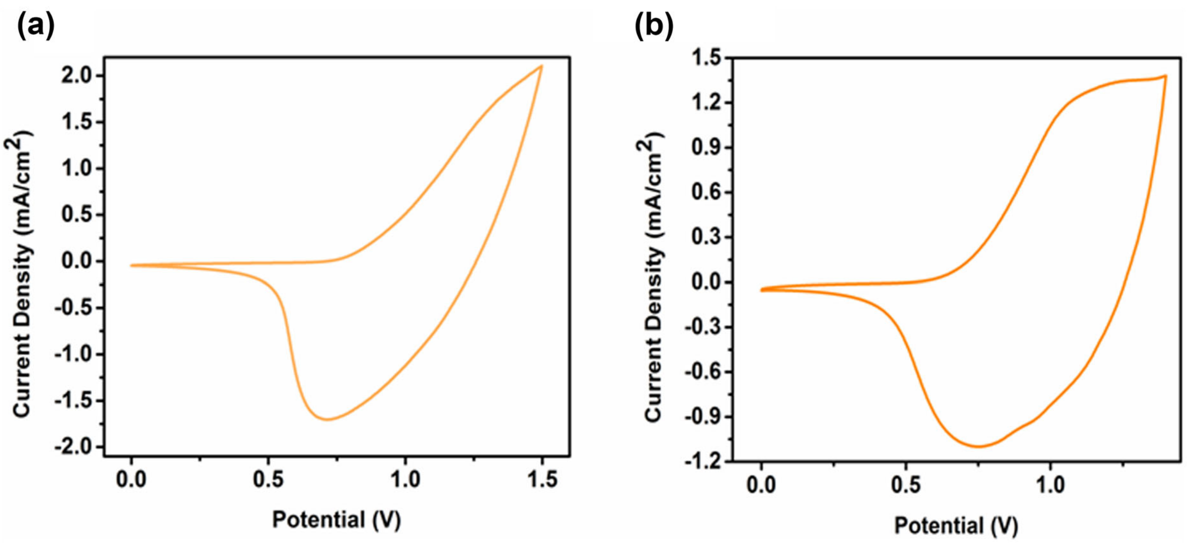


Figure 1. Single-scan cyclic voltammograms of polymers (a) P1, (b) P2 on ITO electrode in 0.1 M $TBAPF_6$/ACN solution at a scan rate of 100 mV s^{-1}.

the obtained crude product was purified by column chromatography. The chemical structures of pure products were determined by FTIR and^{1}H NMR techniques.

2.2.3.1. 1-[4-((2,5-Dibromthiophen-3-ylmethoxy) phenyl] -2-phenyldiazene (6). 1-[4-((2,5-Dibromthiophen-3-ylmethoxy) phenyl] – 2-phenyldiazene was obtained by bromination of 1-phenyl-2- (4-(thiophen-3-ylmethoxy) phenyl) diazene with NBS according to the general synthesis method. The crude product was purified by column chromatography using a solvent mixture of hexane/ethyl acetate (3: 1).

FTIR spectrum (ATR) νmax/cm $^{-1}$: 3069 (thiophene aromatic CH stretch), 3049 (benzene aromatic CH stretch), 2927-2864 (aliphatic CH stretch), 1603,1582 (aromatic C=C stretch), 1497-1367 (aliphatic CH stretch), 1240 (CO stretch).

^{1}H NMR spectrum ($CDCl_3$) δ/ppm: 5.01 (t, 2H), 7.04-7.06 (m, 3H), 7.44-7.52 (m, 3H), 7.87-7 94 (m, 4H).

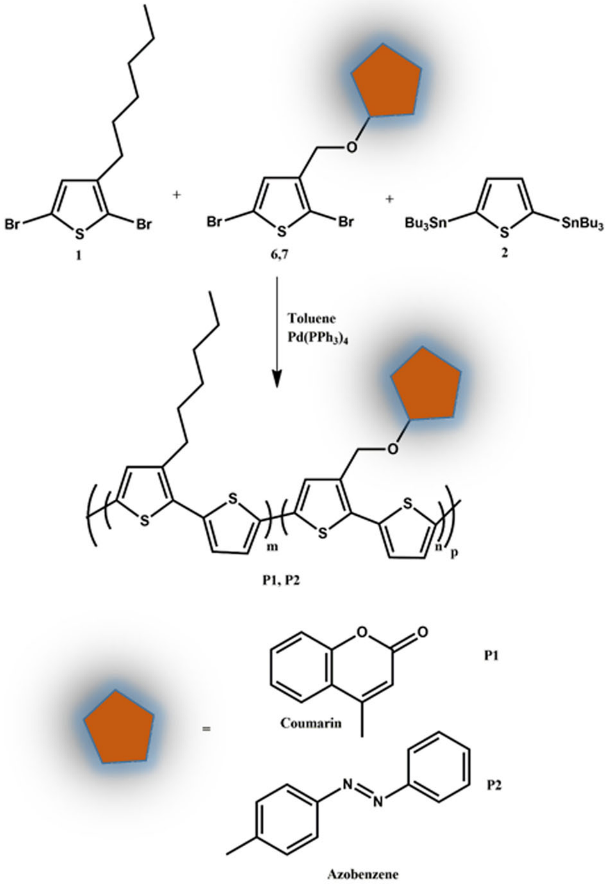
MS (EI): calculated for $C_{17}H_{12}N_2OS$ m/z: 452.1, found m/z: 452 (15), 254.9 (100), 197 (20), 176 (10), 95 (5), 77.1 (40).

2.2.3.2. 4 - [(2,5-Dibromthiophen-3-ylmethoxy)]- 2H-chromen-2-one (7). 4-[(2,5-Dibromthiophen-3-ylmethoxy)]-2H-chromen-2-one was obtained from the bromination reaction of 4-(thiophen-3-ylmethoxy)-2H-chromen-2-one according to the general synthesis method. The crude product was purified by column chromatography with CH_2Cl_2.

FTIR spectrum (ATR) νmax/cm $^{-1}$: 3085 (thiophene aromatic CH strain), 3068 (benzene aromatic CH strain), 2987, 2927 (aliphatic CH strain), 1717, 1704 (C=O strain), 1623-1567 (aromatic C=C stretch), 1492-1330 (aliphatic CH stretch), 1248 (CO stretch).

^{1}H NMR spectrum (CDCl $_3$) δ/ppm: 5.08 (t, 2H), 5.76 (t, 1H), 7.05 (t, 1H), 7.54-7.59 (m, 1H), 7.81-7.83 (d,*J* = 8 Hz and *J* = 1.6 Hz, 1H).

MS (EI): calculated for $C_{14}H_8O_3S$ m/z: 416, found m/z: 416.1 (5), 335 (100), 305 (20), 225 (16), 207 (5), 187.9 (5), 171.1 (10), 135 (25), 120 (8), 107 (16), 92 (20), 63 (20).



Scheme 1. Synthesis of P1 and P2.

2.2.4. Synthesis of P1 and P2 by chemical polymerization method

The dibromthiophene derivatives (6 and 7) containing the chromophore group (0.45 mmol) and 2,5-dibromo-3-hexylthiophene (1) were placed in a 100 mL double ended flask and then completely dissolved in 15 mL of freshly prepared dry toluene. Argon was passed through the reaction medium for 10 minutes. Finally, 2.5-bis (tributylthin) thiophene (2)

(0.91 mmol) and $Pd(PPh_3)_4$ catalyst (0.023 mmol) were added and boiled under reflux. After the reaction was completed, the toluene suspension was cooled to room temperature and poured into 150 mL of methanol. The precipitated solid crude product was filtered off and dried in the air (Scheme 1). The solid product was purified by Soxhlet extraction using methanol, hexane and chloroform, respectively. The chemical structure of the pure product obtained from the chloroform phase was elucidated using FTIR, ^{1}H NMR and elemental analysis techniques.

2.2.4.1. Synthesis of poly (4-((3‴-hexyl-[2,2′:5′,2″:5″,2‴-tetrathiophene]-3′-yl)methoxy) - 2H-chromen-2-one (P1). P1 was obtained according to the general synthesis method by Stille copolymerization reaction of 4-[(2,5-dibromthiophen-3-ylmethoxy)]-2H-chromen-2-one,2,5-dibrom-3-hexylthiophene (1) and 2,5-bis (tributylthin) thiophene (2). The crude product was purified by Soxhlet extraction with 51% yield.

FTIR spectrum (ATR) vmax/cm^{-1}: 3063 (aromatic CH stretch), 2948-2851 (aliphatic CH stretch), 1723, 1621 (C=O stretch), 1608, 1566 (aromatic C=C stretch), 1460-1355 (aliphatic CH bending), 1233 (CO stretch).

Table 1. Electrochemical calculations for P1 and P2.

	$E_{p\text{-}doping}$ (V)	$E_{p\text{-}dedoping}$ (V)	$E^{onset}_{p-doping}$ (V)	HOMO (eV)	LUMO (eV)
P1	1.25/1.35	0.71	0.89	−5.64	−3.76
P2	1.06/1.21	0.75/0.95	0.72	−5.47	−3.83

^{1} H NMR spectrum ($CDCl_3$) δ/ppm: 0.9-1.66 (5 H), 2.77 (1 H), 5.25 (1 H), 5.8 (1 H), 7, 02-7.57 (10 H).

Elemental analysis: ($C_{60}H_{27}O_3S_8$) Calculated % C 66.44; H 5.48. Found % C 65.89; H 5.96.

2.2.4.2. Synthesis of poly (1-(4-((4‴-hexyl-[2,2′: 5′, 2″: 5″, 2‴-tetrathiophene]-3′-yl) methoxy) phenyl) -2-phenyldiazene) (P2). P2 was obtained according to the general synthesis method by Stille copolymerization reaction of 1-[4-((2,5-Dibromthiophen-3-ylmethoxy) phenyl] − 2-phenyldiazene, 2,5-dibrom-3-hexylthiophene (1) and 2,5-bis (tributylthin) thiophene(2). The crude product was purified by Soxhlet extraction with 63% yield.

FTIR spectrum (ATR) vmax/cm $^{-1}$: 3064 (aromatic CH stretch), 2923, 2851 (aliphatic CH stretch), 1599, 1499 (aromatic C=C stretch), 1457, 1362 (aliphatic CH flex), 1232, 1222 (CO stretch).

1 H NMR spectrum ($CDCl_3$) δ/ppm (Annex 1.27.1): 0.89-1.57 (pc, Hb, Hc, Hd, He, Hf), 2.75 (y, Ha), 5.18 (y, Ht), 6.81-7.94 (pc, Hg), Hh, Hi, Hk, Hl, Hm, Hp, Hr, Hs, Hn and Ho).

Elemental analysis: ($C_{84}H_{74}O2S_{10}$) Calculated % C 67.48; H 5.19; N 3.75. Found %; C 68.01; H 4.97; N 3.38.

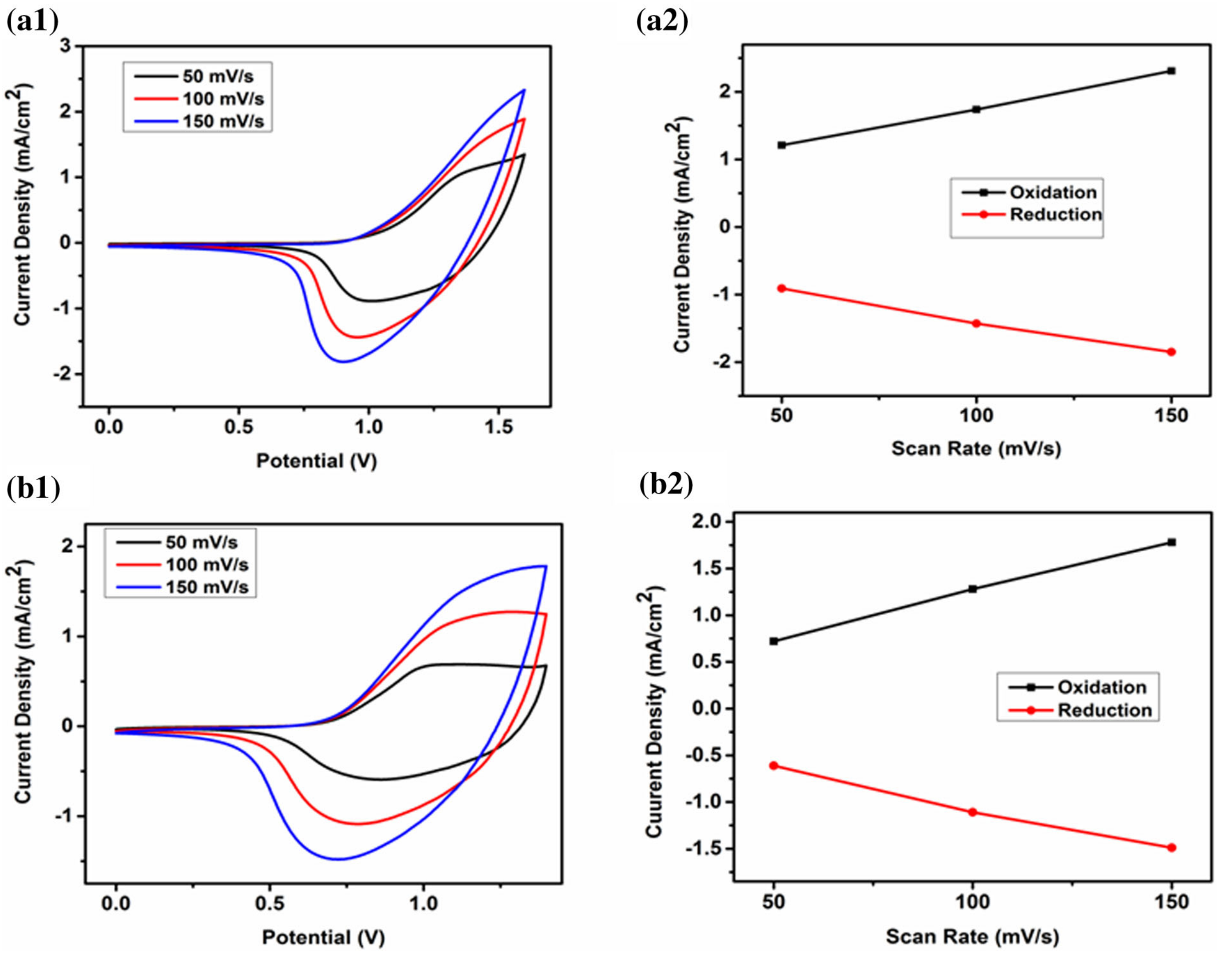


Figure 2. Scan rate dependency of polymers at 50, 100, 150 mV/s (a1, a2) for P1 and (b1, b2) for P2.

3. Results and discussion

3.1. Electrochemical properties

Cyclic voltammetry (CV) is a powerful and popular electrochemical technique that is commonly used for the determination of reduction and oxidation processes of molecular species. It is a very beneficial technique for both electropolymerization and electroactivity determination of the compounds. Also its certain simplicity and numerous advantages make this method applicable in different fields. CV is commonly used for the determination of HOMO-LUMO energy levels and redox potentials. Due to the above-mentioned advantages, all electrochemical properties for both polymers (P1and P2) were determined via CV.

The oxidation potentials were obtained from Fig. 1 and reported as 1.25/1.35 V for P1 and 1.06/1.21 V for P2. The corresponding dedoping potentials were recorded as 0.71 V and 0.75/0.95 V for P1 and P2, respectively. While oxidation and reduction potentials were determined directly from the current vs potential graph, the E_{doping}^{onset} values were determined from the onset of the oxidation potentials as 0.89 V and 0.72 V for P1 and P2 respectively. Another important parameter for conducting polymers is HOMO energy level which can be calculated from CV. HOMO energy levels were calculated as −5.64 eV and −5.47 eV for P1 and P2 from the onset of the corresponding oxidation potentials with Eqn.1 (NHE was taken as −4.75 eV vs. vacuum).

$$HOMO = -\left(4.75 \; + E(ox, onset)\right) \qquad \text{(Eqn. 1)}$$

Table 2. Summary of spectroelectrochemical data for P1 and P2.

	λ_{max} (nm)	$\lambda_{max}{}^{onset}$ (nm)	$E_g{}^{op}$(eV)	Polaron/Bipolaron
P1	440/465	659	1.88	680/1600
P2	475/520	754	1.64	755/1625

Differences in oxidation potentials ($E_{p\text{-}doping}$) which mainly resulted from the different electron densities on polymer chains are important for redox behaviors of the resulting polymers. Band gap (E_g) is the energy difference between the HOMO and LUMO energy levels and can be calculated from electrochemical or spectroelectrochemical characterizations. Both P1 and P2 are only p-type dopable polymers and LUMO levels could not be calculated from reduction potentials so, LUMO energy values were calculated from the $E_g{}^{op}$ and HOMO values as-3.76 eV for P1 and −3.83 eV for P2. All related electrochemical analyses data were summarized in Table 1.

The scan rate dependency of the doping/dedoping processes can be investigated with recording CVs at different scan rates. Three different scan rates (50 mV/s, 100 mV/s and 150 mV/s) are used to investigate the relationship between the peak current and the scan rate. Current density vs potential and current density vs scan rate graphs were recorded at three different scan rates and illustrated in Fig. 2. As seen in Fig. 2, there is a linear relationship between the current density and the scan rate for both polymers. According to this relationship, it is clear that the polymer

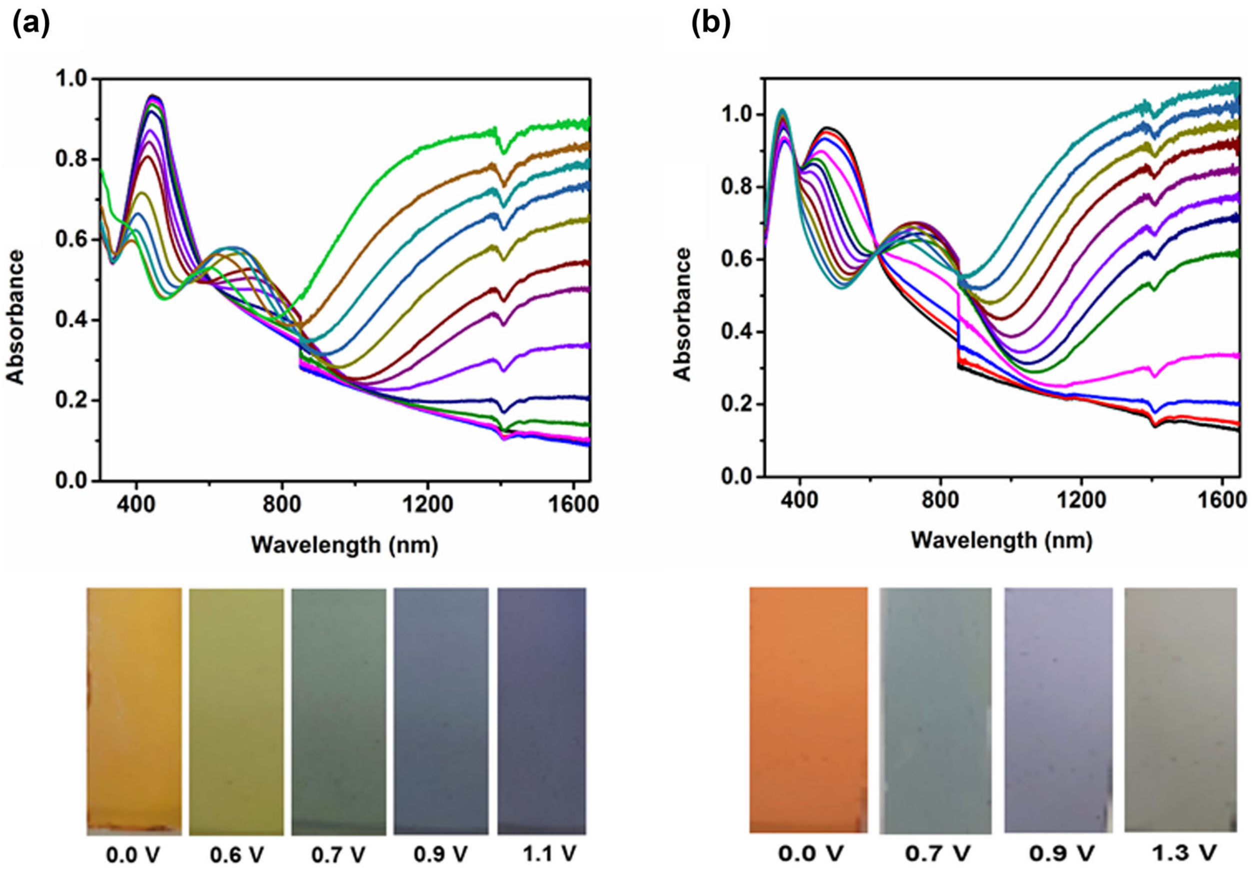


Figure 3. UV-Vis-NIR spectra and colors of (a) P1 and (b) P2 at different potentials.

films were well adhered on ITO electrode and redox processes are non-diffusion controlled.

3.2. Spectroelectrochemical properties

For spectroelectrochemical characterizations, the chemically synthesized P1 and P2 were dissolved in chloroform (5 mg mL^{-1}) and spray-coated onto ITO-coated glass slides. The studies were performed via UV-Vis-NIR spectrophotometer instrument integrated with potentiostat upon applied potentials changing from 0.0 V to 1.3 V. Before applying any potential, true neutral state absorptions were recorded for both copolymers at −0.3 V constant potential. Optical band gap (Eg) and λ_{max} are very important parameters for the characterization of the conjugated polymers and can be calculated from spectroelectrochemical analyses. The corresponding λ_{max} values which can be defined as the maximum absorbance wavelength were observed at 440/465 nm for P1 and at 475/520 nm for P2. $\lambda_{max}{}^{onset}$ values were also calculated from the slope of neutral state absorptions as 659 nm and 754 nm for P1 and P2, respectively. Then, optical band gap ($E_g{}^{op}$) of the resulting polymers were calculated from the onsets of lowest energy π–π^* transition and reported as 1.88 eV for P1 and 1.64 eV for P2 in Table 2. Chemically synthesized thiophene comprising alternating copolymers with azobenzene and coumarin subunits can be compared in terms of optical behaviors, electrochemical and spectroelectrochemical features. As seen in Tables 1 and 2, azobenzene functionalized P2 exhibited lower oxidation potential and lower optical band gap with red shifted neutral state absorption. During spectroelectrochemical analysis, the intensity of neutral state absorption of each copolymer decreases during stepwise oxidation of copolymer films. The formation of newly generated bands upon stepwise oxidation indicates the formation of charge carriers i.e., polarons and bipolarons. Polaron and bipolaron regions were observed at 680 nm and 1600 nm for P1 and at 755 nm and 1625 nm for P2 from Fig. 3. All related spectroelectrochemical data were summarized in Table 2. Additionally, during this p-doping process, while the color of P1 changed between oranges yellow (neutral state) and blue (oxidized state), the color of P2 changed from orange (neutral state) to gray (oxidized state).

Colorimetry studies were carried out to fully express the neutral, oxidized state and intermediate colors of the synthesized copolymers. The colors corresponding to each applied potentials were recorded both for P1 and P2, CIE codes are used to explain these colors scientifically. In this coding system, the brightness of the color is indicated by 'L', the coordinates between red and green is indicated by 'a' and the coordinates between yellow and blue are indicated by 'b'. In the coding system, + b indicates that the color is yellow and -b indicates that the color is blue. In the same way, + a value is used for red and -a value is used for green colors.[25] The corresponding L, a, b coordinates for the synthesized polymers in the CIE coding system are given in Table 3. As mentioned before, P1 showed oranges yellow in neutral state. According to the CIE coding system, b is positively marked and the color in the corresponding coordinate is yellow. The applied potential then changes its oxidized color to blue, which is confirmed by a negative b values. P2, as previously mentioned, is orange in the neutral state. According to the CIE coding system, a and b values with high and positive signs confirm this neutral color. After the applied potential, its color changes to gray in oxidized state. No significant differences in brightness were observed for both polymers.

Table 3. Colorimetric measurements of copolymers (P1 and P2).

Polymer	*Applied Potential (V)*	*L*	*a*	*b*
P1	0.0	68.64	17.32	60.97
	0.6	64.31	−6.77	38.43
	0.7	53.53	−10.23	3.56
	0.9	47.28	−1.73	−12.38
	1.1	41.07	4.95	−15.82
P2	0.0	66.66	40.70	53.24
	0.7	58.42	−6.88	−2.98
	0.9	61.07	4.27	−10.67
	1.3	67.47	0.95	5.13

3.3. Electrochromic contrast and switching studies

It is an important parameter for a material to rapidly change its color between neutral and oxidized states to expand the application areas of electrochromic polymers. For this reason optical contrast and switching times of materials should be calculated. Kinetic studies were performed for determining the optical contrast and switching times at certain wavelengths. In order to determine the electrochromic switching capabilities of the polymer, a square-wave potential step method and spectrophotometer were combined in kinetic studies (Fig. 4). Firstly the polymer was spray coated on ITO and then the potentials were applied between the doped and dedoped states to record the electrochromic switching studies. The switching time of the electrochromic material is the time required for a full switch of between the two extreme states. In the other words, the time is required for the color change of a material between its neutral and oxidized states can be described as a switching time of materials. Optical contrast is defined as the difference in color contrast between two colors. As shown in Table 4, while P1 exhibited 20% (at 455 nm) and 55% (at 1600 nm) optical contrast values upon doping/dedoping processes, P2 had

Table 4. Summary of kinetic studies of polymers.

	Wavelength (nm)	*Optical Contrast (T %)*	*Switching Times Oxidation (s)*	*Switching Times Reduction(s)*
P1	455	20	3.3	1.9
	1600	55	2.7	2.8
P2	510	29	2.0	1.7
	1625	62	1.9	2.0

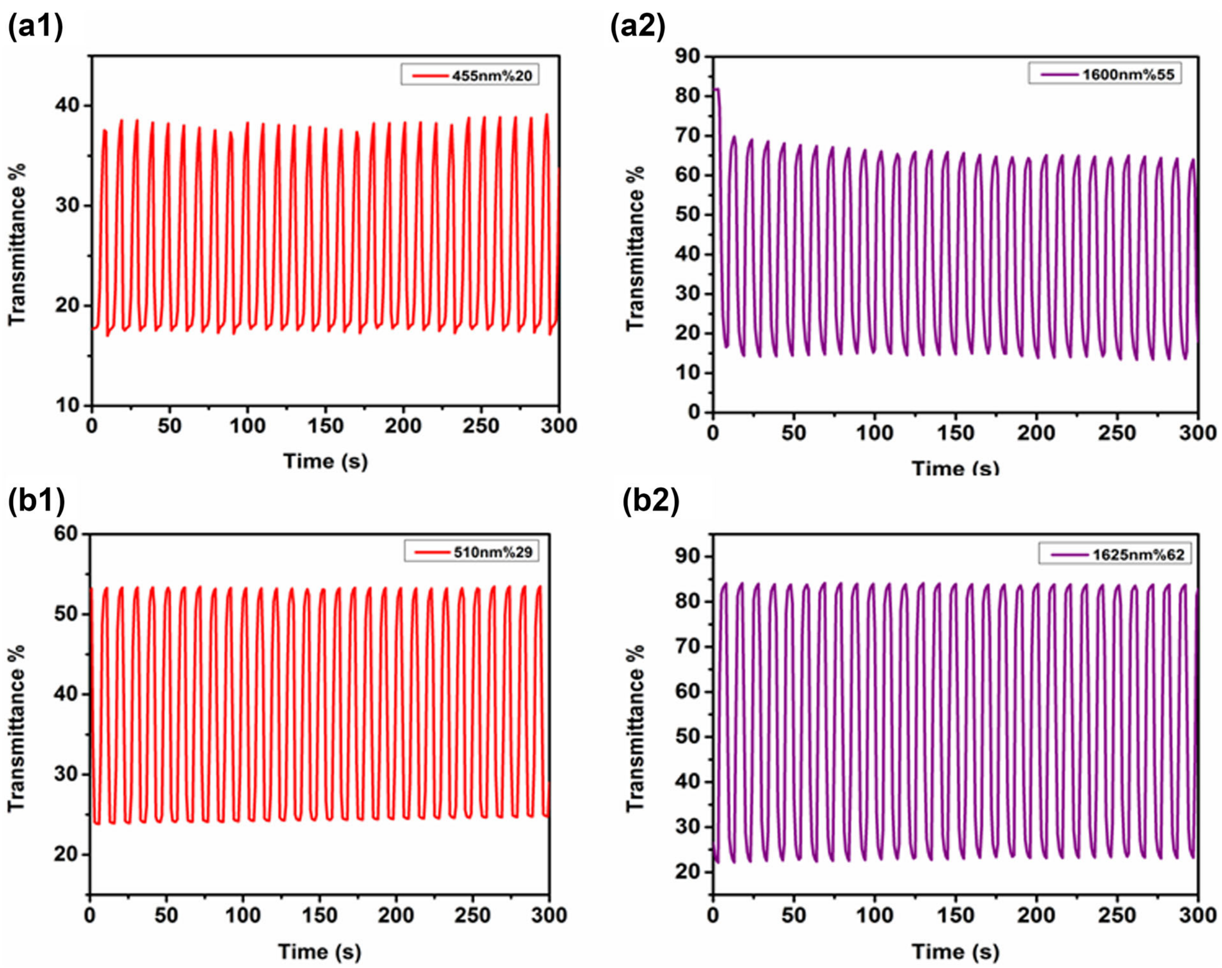


Figure 4. Percent transmittance changes of (a) P1, (b) P2 at different wavelengths.

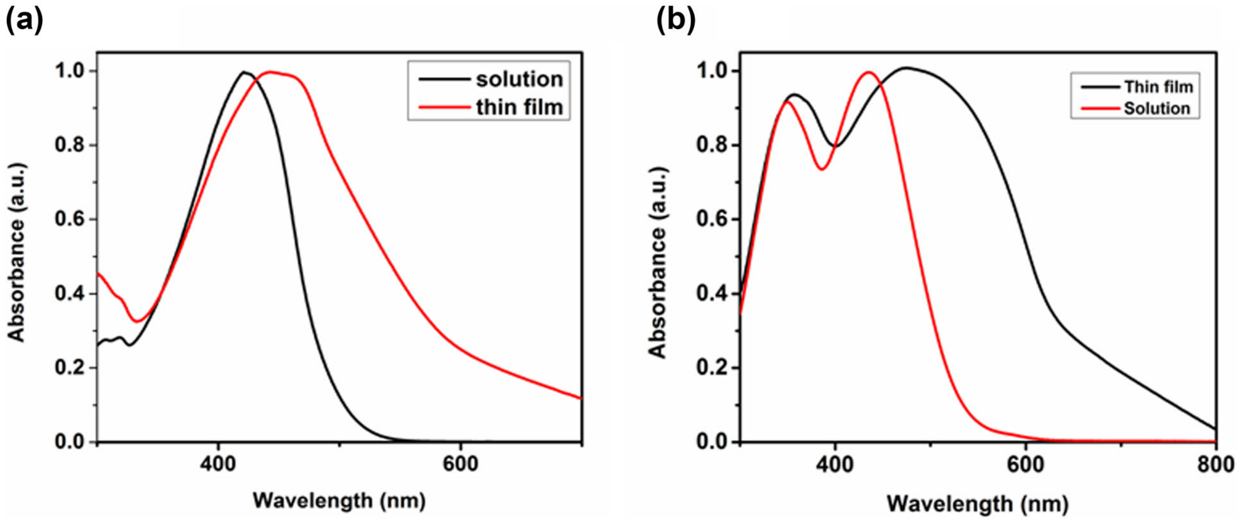


Figure 5. Absorption spectra of (a) P1 and (b) P2 in thin film and chloroform solution.

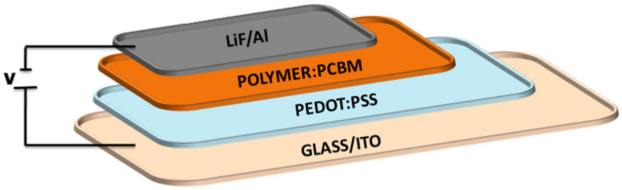


Figure 6. Schematic representation of device configuration.

29% and 62% optical contrasts at 510 nm and at 1625 nm, respectively. Switching times during oxidation were reported as 3.3 s and 2.7 s for P1 and 2.0 s and 1.9 s for P2, and those for reduction were reported as 1.9 s and 2.8 s for P1 and 1.7 s and 2.0 s for P2 at corresponding wavelengths. Electrochromic contrast and switching studies show that P2

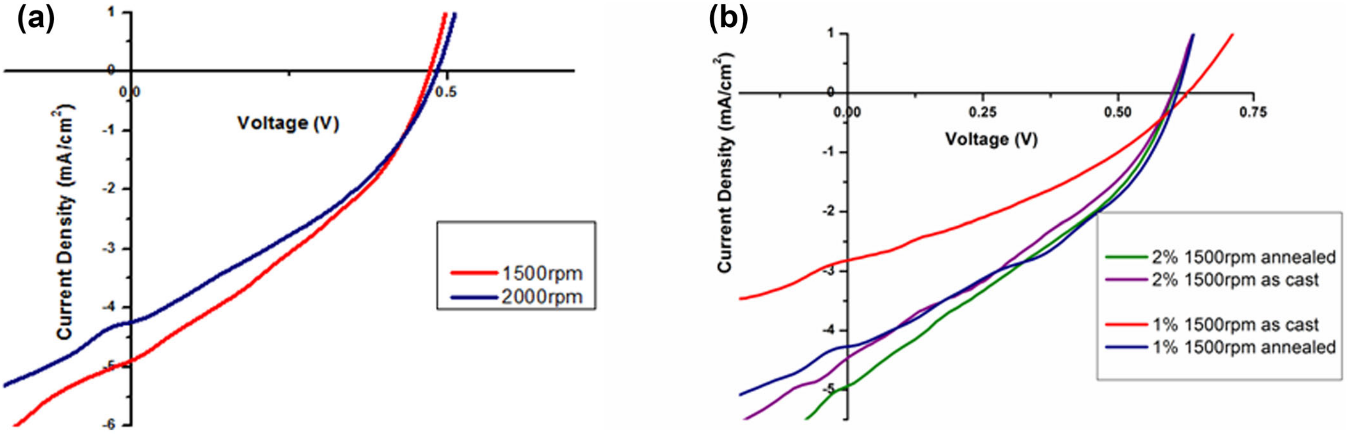


Figure 7. Photovoltaic properties of bulk heterojunction OSCs based on, a) P1: $PC_{60}BM$ (1:1) in 2% chloroform solution, b) P2: $PC_{60}BM$(1:1) in 1% and 2% chloroform solution.

Table 5. Photovoltaic properties of bulk heterojunction OSCs based on P1:$PC_{60}BM$ and P2: $PC_{60}BM$ in a ratio of 1:1.

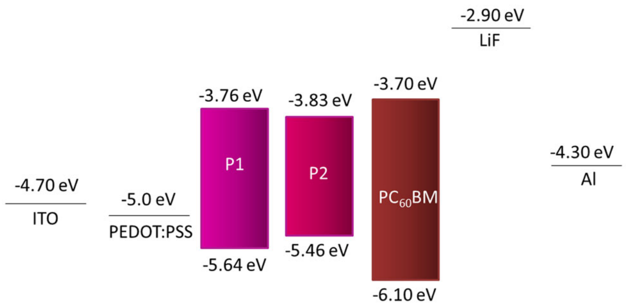
		Voc (V)	Isc (mA/cm^2)	FF	η(%)
P1	2%1500 rpm	0.47	4.92	0.35	0.81
	2% 2000 rpm	0.49	4.26	0.36	0.75
P2	1% 1500 rpm as cast	0.63	2.81	0.33	0.58
	1% 1500 rpm annealed	0.61	4.29	0.33	0.63
	2% 1500 rpm as cast	0.60	4.47	0.32	0.86
	2%1500 rpm annealed	0.60	4.98	0.32	0.96

has a lower switching time values than P1. It can be due to the increasing length of spacer unit because of the improved ion diffusion and dopant insertion. According to electrochemical, spectroelectrochemical and kinetic results, these thiophene bearing alternating copolymers with Azobenzene and Cumarin subunits can be used in the construction and the development of electrochromic devices and organic solar cells.

The normalized absorbance spectra for both polymers in both solution and thin film form are illustrated in Fig. 5. While P1 showed absorption in the visible region centered at 420 nm and P2 centered at 350 nm/440 nm in solution, P1 showed absorption centered at 450 nm and P2 exhibited absorption centered at 360 nm/490 nm in thin film form. These obvious red shifted absorptions in the thin film form could be explained with the reduced solvent-monomer interactions and the tendency to accumulate in thin film form compared to those in the solutions.

3.4. Photovoltaic properties

Before the organic solar cell (OSC) fabrication, the ITO electrodes were cleaned in an ultrasonic bath for 15 minutes with detergent, deionized water and isopropyl alcohol. Then oxygen plasma cleaning was performed. PEDOT:PSS layer was filtered with 0.45 μm pore size filter and coated on ITO electrode. The PEDOT/PSS layer was coated and heated and dried on a hot plate at 135 °C for 15 minutes. Polymer (P1 and P2):PCBM mixtures were prepared and stirred overnight then filtered through 0.2 μm PTFE, this mixture was coated via spin-coating in a nitrogen-filled glove box and. As a final step in the construction of this solar cell, lithium fluoride (0.8 nm) and aluminum (100 nm) were coated onto the active layer under high vacuum.



Scheme 2. Energy band diagram for ITO/PEDOT:PSS/P1 and P2/$PC_{60}BM$/LiF/Al.

Performances of PSCs based on P1 and P2 were investigated with the device structure of ITO/PEDOT:PSS/Polymer(P1/P2):$PC_{60}BM$/LiF/Al (Fig. 6). $PC_{60}BM$ was used as the acceptor for organic solar cell device construction and PEDOT:PSS was coated on an ITO electrode as hole transport layer. PEDOT:PSS layer both satisfy the smoothing of the ITO electrode surface and increase the work function of ITO (Scheme 2).

Organic solar cell applications highly depend on solubility and film formation of the polymer fullerene blend hence, the proper solvent selection is a very important parameter in the construction of well performance device, thus proper solvents were selected for both copolymers to construct the device with the desired properties. While the P1-$PC_{60}BM$ blends were prepared in 2% chloroform solution, the P2-$PC_{60}BM$ blends were prepared in 1% and 2% chloroform solutions. After solvent optimization, polymer: $PC_{60}BM$ weight ratios were optimized as 1:1 for both P1:$PC_{60}BM$ and P2: $PC_{60}BM$. Optimization studies were performed exploring the effect of concentration and thermal annealing for P2. In this optimization study, the polymer and $PC_{60}BM$ mixture was prepared in 1% and 2% chloroform solution and coated on ITO at both 1000 rpm and 1500 rpm. While one of the cells was annealed, the other remained as cast to investigate the annealing effect on resulting organic solar cell. As summarized in Table 5, P1 and $PC_{60}BM$ comprising solution was prepared with 1:1 ratio, in 2% chloroform solution and coated on ITO at 1500 rpm and 2000 rpm and finally 0.8 nm

LiF and 100 nm Al metals were coated on the active layer. Optimum annealing temperature and time were determined as 90 °C and 5 minutes. Related J-V curves of the solar cells are represented in Fig. 7.

From these J-V curves, Voc, Jsc, FF values and the power conversion efficiency, η (%), values of organic solar cells were calculated. Voc value is an open circuit voltage and can be measured as the potential at the zero current through the cell. J_{sc} of the cell is the short circuit current and can be measured as the current at the zero potential. The FF value is a variable used to define the maximum output power of a PV cell based on open circuit voltage and short circuit current. η is the power conversion efficiency obtained from the solar cell and is calculated from Voc, Isc and FF values. For P2: $PC_{60}BM$ (1:1) comprising OSCs, the effect of the solution concentration and the annealing on the power conversion efficiency of the cell were investigated and the best performed cell exhibited 0.96% efficiency with 0.60 V and 4.98 mA/cm^2, Voc and Isc values at 2% chloroform solution and after annealing was performed at 90 °C for 5 minutes. For P1:$PC_{60}BM$ (1:1) comprising OSCs, the best performed device exhibited 0.81% efficiency with 0.47 V, V_{oc} and 4.92 mA/cm^2 I_{sc}, values. All results are summarized in Table 5. After the annealing was performed at 90 °C for 5 minutes, results for P2: $PC_{60}BM$ (1:1) comprising OSCs showed the highest photovoltaic performances (Table 5). As seen, annealing processing improved PCE from 0.86% to 0.96% for P2.

Electrochemical and spectroelectrochemical properties of synthesized copolymers illustrated that P2 absorbed in the narrower range with lower optical band gap and higher optical contrast values. Additionally, the color transitions are more pronounced and the switching time is lower for P2. In terms of OSC studies, it was observed that P2 based OSCs had higher power conversion efficiency compared to the P1 comprising ones.

4. Conclusion

Azobenzene and coumarin functionalized thiophene comprising copolymers (P1 and P2) were designed and synthesized with thiophene bridge via chemical polymerization techniques to use in the electrochromic and organic solar cell applications. Stille coupling reactions were used to synthesize polymers P1 and P2. Characterizations, electrochemical and spectroelectrochemical analysis of the resulting copolymers were carried with NMR, FTIR, elemental analysis, Cyclic voltammetry (CV) and UV-Vis spectrophotometer techniques. P1 and P2 showed appropriate electrochemical, spectroelectrochemical and optical behaviors for photovoltaic and electrochromic applications. Both copolymers exhibited multichromic behavior with neutral state orange colors and the optical band gap values were 1.88 eV/1.64 eV for P1 and P2, respectively. When the different potentials are applied color changes occur and finally the color of P1 turns blue and the color of P2 turns gray. The HOMO and LUMO values were determined using cyclic voltammetry as −5.64 and −3.76 eV for P1 and −5.47 and −3.83 eV for P2, respectively. Kinetic studies were performed for determination of the optical contrast and switching times which are used for color changes at certain wavelengths. P1 exhibits 20% and 55% optical contrast values at 455 nm and 1600 nm upon doping/dedoping processes. P2 has 29% and 62% optical contrasts at 510 nm and 1625 nm, respectively. Switching times during oxidation were reported as 3.3 s and 2.7 s for P1 and 2.0 s and 1.9 s for P2, and those for reduction were reported as 1.9 s and 2.8 s for P1 and 1.7 s and 2.0 s for P2 at corresponding wavelengths. According to obtained analyses results of the preliminary organic solar cell applications were performed and performances of PSCs based on P1 and P2 were investigated with the device structure of ITO/PEDOT:PSS/Polymer(P1/P2):$PC_{60}BM$/LiF/Al. As a result of the optimization studies, the highest power conversion efficiency was obtained as 0.81% for P1 based device with 0.47 V Voc and 4.92 mA/cm^2 Isc values. The highest efficiency for P2 comprising device was found to be 0.96% under optimum conditions with 0.60 V and 4.98 mA/cm^2, Voc and Isc values, respectively. In order to increase these yield percentages obtained from synthesized polymers, we continue to work in the laboratory.

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