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Syntheses, characterizations and electrochromic applications of polymers derived from carbazole containing thiophene rings in side chain with electrochemical and FeCl₃ methods

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ABSTRACT

1,8-Bis(3,6-di(thiophen-3-yl)-9*H*-carbazol-9-yl)octane (BDTCO) was synthesized via Ullmann and Suzuki couplings. Additionally, its homopolymer and copolymers with 3,4-ethylenedioxythiophene (EDOT), pyrrole (Py) and thiophene (Th) were synthesized and coated onto an ITO-glass surface via electrochemical oxidative polymerization. The spectroelectrochemical and electrochromic properties of the polymers were also investigated. The switching ability of these polymers was measured as the percent transmittance (*T*%) at their point of maximum contrast. Moreover, the polymer of BDTCO (P-BDTCO) was successfully synthesized through FeCl₃ oxidative polymerization. The compounds were characterized by FT-IR, NMR and X-ray Photoelectron Spectroscopy (XPS), and their thermal stabilities were determined via TG measurements. The solid state conductivities of the polymeric films coated onto the ITO-glass surface were measured via the four point probe technique using an electrometer. In addition, the surface morphological properties were investigated by Scanning Electron Microscopy (SEM) for different magnifications.

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1. Introduction

Most low band gap polymers have synthesized via Suzuki [1–3], Yamamoto [3] and Stille [4,5] coupling polymerizations. Compared with these polymerization methods, ferric (III) chloride (FeCl₃) oxidative polymerization is easy and cheap with mild reaction conditions (at room temperature), thereby making it suitable for large scale production [6], and gives high molecular weight polymers. Polymerization with FeCl₃ has up to now been reported to produce irregular polymers only [7]. The standard procedure is to suspend FeCl₃ in chloroform and then add the thiophene monomer quickly [8]. Additionally, many π -conjugated polymers have recently been synthesized via electropolymerization [9–11]. Electrocopolymerization process carries out by combining with different

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1566-1199/\$ - see front matter \odot 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.orgel.2012.12.023 structured co-monomers. Contrary to synthetic approach, copolymerization is an easy and facile method to combine the electrochromic properties of the parent polymers [12]. In literature there are several studies that investigate copolymerization and tune the color of the conducting polymers via copolymerization. Among that utilization of 3,4ethylenedioxythiophene (EDOT) has dominated literature owing to EDOT's rapid switching ability and high stability. Since most of the conducting polymers display color variations simply between two colors, it is crucial for potential applications to obtain a multichromic conducting polymer with short switching time and high stability. Moreover, an electrochromic material is one that changes color in a persistent but reversible manner by an electrochemical reaction, and the phenomenon is called electrochromism [13]. A number of conjugated polymers have colors both in the oxidized and reduced states. The color exhibited by the polymer is determined by the band gap energy (E_g) , defined as the onset of the π - π ^{*} transition.



In this paper, we primarily aimed to investigate the effects of the copolymers with pyrrole (Py), thiophene (Th) and 3,4-ethylenedioxythiophene (EDOT) of 1,8-bis(3,6di(thiophen-3-vl)-9H-carbazol-9-vl)octane (BDTCO). which has the aliphatic groups on electrochromic properties. Additionally, we reported electrochemically the synthesis of new polymers containing carbazole moieties with aliphatic groups, Py, EDOT and Th units. The most widely used method is the coating of the electrode with a monomer and then performing electropolymerization in the presence of a co-monomer. For this purpose, 1,8-bis(3,6-dibromo-9H-carbazol-9-yl)octane (BDBCO)) was firstly synthesized using an Ullmann coupling [14]. Then, 1,8-bis(3,6-di(thiophen-3-yl)-9H-carbazol-9-yl)octane (BDTCO) was synthesized using a Suzuki coupling [15]. Moreover, the oxidative polymer of BDTCO (P-BDTCO) was performed by the oxidative polymerization reaction with ferric (III) chloride (FeCl₃). The structures of the synthesized polymers were confirmed by using FT-IR, ¹H NMR and CV techniques. Also, thermal stabilities of the polymers were investigated. The conductivities of electrochemically prepared polymer films were measured on pellet at solid state for P-BDTCO and the electrode surface for electrochemically the synthesized polymers via the fourprobe technique at room temperature. The obtained results showed that the synthesized copolymers could be used for electrochromic applications.

2. Experimental section

2.1. Materials

Carbazole, N-bromosuccinimide (NBS), 1,8-dibromopentane, ferric (III) chloride (anhydrous) (FeCl₃) and Aliquat 336 were supplied from Alfa Easer Chemical Co. (Germany). 3-Thiophene boronic acid, Cul and 18-Crown-6 were supplied from Across Chemical Co. (USA). [Pd(PPh₃)₄], pyrrole (Py), thiophene (Th) and 3,4-ethylenedioxythiophene (EDOT) were supplied from Aldrich Chemical Co. (USA). SiO₂, K₂CO₃, N,N'-dimethylacetamide (DMA), dichloromethane (DCM), methanol, chloroform (CHCl₃), hexane, toluene, acetonitrile (AN) were supplied from Merck Chemical Co. (Germany) and used as received. Boron trifluoride ethyl etherate (BF₃EtE) was supplied from Fluka Chemical Co. Silica gel was used as an efficient and reusable catalyst.

2.2. Syntheses of the beginning compounds and monomer (1,8-bis(3,6-di(thiophen-3-yl)-9H-carbazol-9-yl)octane (BDTCO))

3,6-Dibromocarbazole, the aliphatic bridged compound with tetra Br groups (1,8-bis(3,6-dibromo-9H-carbazol-9-yl)octane (BDBCO)) containing carbazole units and 1,8-bis(3,6-di(thiophen-3-yl)-9H-carbazol-9-yl)octane (BDTCO) were synthesized as reported in the literature (Yield ~60%) [10,16]. The obtained compounds have different colors. For example, the aliphatic bridged compound with tetra Br groups is a light yellow colored; BDTCO is a dark brown colored. The synthesis pathways are shown in Scheme 1.

For BDTCO: ¹H NMR (DMSO): δ_H ppm, 8.48 (s, 4H, Ha, Ha'), 7.84 (s, 4H, Hd, Hd'), 7.68 (d, 4H, Hf, Hf'), 7.58 (m, 12H, Hb, Hb', Hc, Hc', He, He'), 4.33 (t, 2H, Hg, Hg'), 3.37 (m, 2H, Hi, Hi'), 2.52 (m, 2H, Hj, Hj'), 1.24 (m, 2H, Hk, Hk').

2.3. Synthesis of the polymers

2.3.1. Synthesis of P-BDTCO by the FeCl₃ oxidation method

To a suspension of FeCl₃ (162 mg, 1 mmol) in chloroform (5 mL), compound BDTCO (77 mg, 0.1 mmol) in chloroform (5 mL) was added in one portion under argon atmosphere. The reaction was left stirring for 72 h at room temperature. The reaction mixture was then diluted with chloroform and washed with water. The organic phase was then separated and stirred with ammonia (aq. 20%, 100 mL \times 2) for 30 min, followed by washing with 0.2 M ethylene-diamino-tetra-acetic acid (EDTA) solution (50 mL \times 2) and water (200 mL \times 2). The solution was then poured into methanol and the precipitate was collected by centrifugation. After process, the polymer was obtained as a red solid (98 mg, 65%). The synthetic route is shown in Scheme 2 [17].

2.3.2. Electrochemical copolymerization of BDTCO with EDOT, Py and Th

Cyclic voltammetry (CV) measurements were performed using a CHI 660 C Electrochemical Analyzer at a potential scan rate of 0.25 V/s. CV was employed to assay the electrical activity of the compounds and determine their oxidation-reduction peak potentials. Additionally, the copolymers were separately obtained in the presence of Th, Py and EDOT. The system consists of a CV cell containing an indium tin oxide (ITO)-coated glass plate as the working electrode, platinum wire as the counter electrode and Ag wire as the reference electrode. The measurements were performed using a (0.1 M) LiClO₄/acetonitrile (AN:BF₃EtE) (9:1, v/v) solvent mixture at room temperature under an argon atmosphere [18]. The electropolymerizations involved dissolving BDTCO (1 g L^{-1}) in 10 mL of 0.1 M AN/LiClO₄:BF₃EtE (9:1, v/v) and placing the resulting solution into the CV cell before adding 4 mg of Th or Py or EDOT. Next, the solution was repeatedly scanned in the range of the different potentials for each measurement (scan rate: 0.25 V/s and cycle number: 20, respectively). The resulting copolymer and homopolymer films were washed with AN to remove LiClO₄ and BF₃EtE. The homopolymer film of the synthesized monomer was also deposited onto an ITO glass plate using a similar method for comparison (cycle number: 20, scan rate: 0.25 V/s). Scheme 3a and b shows the general electrocopolymerization reaction with Py or Th or EDOT and the chemical structures of the copolymers, respectively.

2.4. Structural characterization techniques

The FT-IR spectra were recorded using a Perkin Elmer FT-IR Spectrum One via using ATR system (4000–650 cm⁻¹). ¹H NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were also recorded using DMSO-d₆ as the solvent at 25 °C. Tetramethylsilane was used as an internal standard. The ob-



Scheme 1. Synthesis of the compounds.



Scheme 2. The oxidative polymerization reaction of BDTCO with FeCl₃.

tained copolymer film was characterized by X-ray Photoelectron Spectroscopy (XPS) measurement (PHI 5000 XPS) which was carried out using mono-chromatic Al Anode by increasing 1 eV. A CHI 660 C Electrochemical Analyzer (CH Instruments, Texas, USA) was used to supply a constant potential during the electrochemical syntheses and cyclic voltammetry experiments. An Analytikjena Specord S 600 single beam spectrophotometer was used for the spectroelectrochemical studies and characterization of the copolymers. The electrical conductivities of electrochemically deposited films of the polymers on ITO-glass plates were measured. These measurements were conducted using on a Keithley 2400 Electrometer using the four point probe technique at 25 °C. The TG-DTA data were recorded using a Perkin Elmer Diamond Thermal Analysis system. The compounds were scanned between 20 and 1000 °C (in N₂, rate 10 °C/min). Additionally, DSC analysis of P-BDTCO was carried out by using Perkin Elmer Pyris Sapphire DSC. DSC measurement was performed between 25 and 420 °C (in N2, rate 20 °C/min). Scanning electron microscopy (SEM) photographs of the compounds were recorded using a Philips XL-305 FEG SEM instrument.

2.5. Spectroelectrochemical studies

Both the co- and homopolymer films, which had been electrochemically deposited onto ITO-coated glass slides, were used to perform the spectroelectrochemical experiments. Spectroelectrochemical and electrochromic measurements were conducted in an LiClO₄/AN solution using an Ag wire as the reference and a Pt wire as the auxiliary electrode. The data obtained from the cyclic voltammetry measurements were used for the spectroelectrochemical measurements of the copolymer and homopolymer films [19]. These measurements were performed to account for the absorption spectra of the copolymer and homopolymer films under the applied potentials. A spectroelectrochemical cell includes a quartz cuvette, an Ag wire (RE), a Pt wire and the polymer film on ITO/glass as a transparent working electrode (WE). These measurements were performed in a



Scheme 3. (a) Electrocopolymerization of BDTCO with Py, Th and EDOT and (b) general presentation of the copolymers.

 $0.1\ M$ LiClO $_4$ supporting electrolyte in AN, as emphasized above.

2.6. Conductivity measurements

Conductivities of the synthesized polymers were measured on a Keithley 2400 Electrometer, using four point probe technique. Instrument was calibrated with ITO glass plate. Iodine doping was carried out by exposure of the polymer films to iodine vapor at atmospheric pressure in a desiccator at 25 °C [20,21].

3. Results and discussion

3.1. Structural characterization

The FT-IR spectra of the synthesized compounds are given in Fig. 1. Fig. 1a shows the FT-IR spectra of BDBCO, BDTCO and P-BDTCO, which possess the aliphatic peaks

and aromatic C–H peaks, respectively. The aliphatic and aromatic C-H peaks are observed at 3073; 2927 and 2850 cm⁻¹, respectively, for BDBCO. The FT-IR spectrum from BDBCO shows that the peak at 730 cm^{-1} related to -Br groups disappears after the reaction, as expected. Similarly, the aliphatic and aromatic C-H peaks are observed at 3048; 2927 and 2850 cm⁻¹, respectively, for BDTCO. The peak at 794 cm^{-1} and widespread peaks are differently observed at the spectrum of BDTCO, when compared with BDBCO. Additionally, the peak at around 1620 cm⁻¹ is related to -NH bending groups in the carbazole units. Also, the polymer (P-BDTCO) synthesized with FeCl₃ method has the aliphatic and aromatic peaks at its spectrum. As seen in its spectrum, the aliphatic and aromatic peaks are obtained at 3023; 2922 and 2846 $\rm cm^{-1}$, respectively. The widespread peak at around 3200 $\rm cm^{-1}$ represents the O-H stretching vibrations due to humidity in the structure of the monomer [22]. The peak related to C--C coupling due to the polymerization appears at 1204 cm⁻¹, as expected (see Fig. 1a). Moreover, C-S stretching is observed



Fig. 1. The FT-IR spectra of (a) BDBCO, BDTCO and P-BDTCO, and (b) BDTCO-co-Th, BDTCO-co-Py and BDTCO-co-EDOT.

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at 799 cm⁻¹, as reported in the literature [11,23]. Fig. 1b shows FT-IR spectra of the electrochemically synthesized copolymers. The FT-IR spectrum from BDTCO-co-Th shows the following absorption peaks: 3088 cm⁻¹ (from the aromatic C–H stretching), 1537 and 1469 cm⁻¹ (from the C=C stretching) and 1208 cm⁻¹ (from the C–N stretching). The broad band observed at approximately 1648 cm⁻¹ proves the presence of polyconjugation, and the peaks at 2926 and 2850 cm^{-1} are related to the aliphatic moieties. The coupled C–C stretching and C–S stretching appears at 1046 cm^{-1} and 796 cm^{-1} , respectively. The spectrum of BDTCO-co-Th includes the characteristic peaks like the aliphatic and coupled C-C vibration peaks. This explains that to be available both thiophene as co-monomer and BDTCO as monomer in the structure of the copolymer. Additionally, as seen in the spectrum of BDTCO-co-Py, it shows the following absorption peaks: 3103 cm⁻¹ (from the aromatic C–H stretching), 2941 and 2875 cm⁻¹ (from the aliphatic C–H stretching), and 1532 cm^{-1} (from the C=C stretching) and 1201 cm^{-1} (from the C–N stretching). The coupled C—C stretching and C–S stretching appears at 1036 cm⁻¹ and 783 cm⁻¹, respectively. According to the spectrum of BDTCO-co-EDOT, the absorption peaks are obtained as follows: 3053 cm⁻¹ (from the aromatic C–H stretching), 2962 and 2881 cm⁻¹ (from the aliphatic C–H stretching), 1580 and 1490 cm^{-1} (from the C=C stretching) and 1269 cm⁻¹ (from the C–N stretching). The coupled C–C stretching and C–S stretching appears at 1160 cm⁻¹ and 718 cm⁻¹, respectively. The intensity of the absorption band at 718 cm⁻¹ from the C-Ha stretching of the thiophene moiety in the monomer appear completely, which is indicative of polymerization at the 2, and 5 positions on the thiophene moiety in the monomer and EDOT (see Fig 1b). Consequently, the results of these FT-IR studies clearly indicate that copolymerization reactions with Py, Th and EDOT and also, the polymerization process with FeCl₃ are successfully achieved.

¹H NMR measurement of BDTCO is performed in DMSO solution because of it is completely soluble in DMSO. The molecular structure of BDTCO is also characterized by ¹H NMR spectrum using DMSO- d_6 as the solvent and the ¹H NMR spectrum of BDTCO is shown in Fig. 2. As seen in Fig. 2, it shows resonance signals for protons from the thiophene, protons related to the aliphatic and benzene rings [24]. Thiophene and carbazole groups have three signals, respectively. According to these data, the characteristic signals at 8.48, 7.58 and 7.56 ppm are attributed to the carbazole moieties, which indicate the reaction has gone to completion. Additionally, the peaks at 7.84, 7.68 and 7.61 ppm are related to the thiophene groups and the other characteristic peaks are the aliphatic peaks at 4.33, 3.37, 2.52 and 1.24 ppm in the monomer structure. This result completely explains the monomer structure. According to the obtained spectral data, the aimed product is successfully obtained.

In order to evaluate the surface composition state of the synthesized polymer (P-BDTCO), XPS investigation was carried out. Thus, intensity scale related to binding energy levels of P-BDTCO is given in Fig. 3 and also, atomic% values are shown as insert data in Fig. 3. As seen in Fig. 3, the signal related to C1s is observed at 284 eV. C1s component at

about 284 eV is mainly due to carbon atoms belonging to aromatic carbon groups of the polymeric conjugated backbone [25]. The peak at 284 eV is attributed to the C--C bonding irrespective of the type of hybridization. Alike C1s core level signals, N1s signal appears at around 336 eV, as expected. This peak related to N1s is assigned to the nitrogen atoms of carbazole units. The energy position of the nitrogen (336 eV) is indicative of C-N bonding [26]. 2s and 2p core levels related to S atom have the signals at 227 and 152, respectively. This shows that monomer units containing thiophene rings are available in the polymer structures, as expected. Additionally, O1s signal is observed at around 530 eV. This explains that oxidize the polymer layer. Moreover, as seen in XPS spectrum of the synthesized polymer, there are various contaminants at particular ratios. For example, O1s core level is observed at ratio of 36.5%. This is guite high in the polymer chains. It is assumed that this peak related to O atom comes from humidity in the structure of the polymer. Before, we touched on humidity in the FT-IR department of the structural characterization section. A widespread peak at around 3200 cm⁻¹ corresponding to humidity is observed in the FT-IR spectrum of P-BDTCO, as emphasized above. Resultantly, the results obtained from XPS of the polymer (P-BDTCO) are in good agreement with those from its FT-IR spectrum.

3.2. Electrochemical properties

Thiophene derivatives readily undergo a one-electron oxidation to form a radical cation (polaron) when their α -positions are unsubstituted. Continual oxidation affords higher ordered oligomers via a radical coupling mechanism that ultimately forms a polymer [27]. The cyclic voltammogram of P(BTDCO) in an AN/LiClO₄ solvent/ electrolyte solution possesses two consecutive oxidation peaks at 1.07 and 1.39 V, and a widespread reduction peak at around 0.5 V when scanned from 0 to +1.8 V. This reduction has been observed for other polymers and may be due to sequential reduction of dicationic bipolaronic charge carriers initially to cation radical polaronic charge carriers and then to neutral polymer or may be due to the ion transport properties of the polymer [28]. As seen in Fig. 4, the first oxidation peak is observed at 0.99 V. This value shifts to 1.07 V in the repeated cycles, and a new oxidation peak at 1.07 V occurs. Additionally, the second oxidation peak is observed at 1.35 V and after the repeated cycles, this value shifts to 1.30 V. A new reduction coupling appeared at a lower potential (E_{ox} = 0.99 V and E_{red} = 0.5 V), which can be attributed to the oxidative doping (i.e., polaron and bipolaron formation) and reductive dedoping of the formed polymer [29]. The decreased oxidation potential after repeated scans is evidence of the electropolymerization, the formation of a polyconjugated structure and a reduction in the electrochemical band gap. The decreasing in the peak current after repeated scans occurs because of polymer adsorption onto the electrode surface, which causes a sensitivity decrease in the electrode. To investigate the CV behavior of BDTCO-co-Th, we performed CV studies in the presence of thiophene between -0.2 and +1.6 V potentials (see Fig. 4). It can be seen the voltammo-



Fig. 2. ¹HMR spectrum of BDTCO.

grams change drastically when compared with the voltammograms related to both P(BDTCO) and thiophene [11]. According to the obtained cyclic voltammogram data, the oxidation peaks at 0.62 and 0.12 V, and the reduction peaks at 0.56 and 0.84 V are observed, respectively. Moreover, there is an incremental increase at consecutive cycle numbers and the oxidation potential of BDTCO-co-Th and they are different from those of either the monomer or pure thiophene, as emphasized above. An incremental increase at consecutive cycle numbers is observed in the cyclic voltammogram of BDTCP-co-EDOT when scanned in the range of -1 and +1.6 V. During the growth of the BDTCO-co-EDOT film, the decreasing in the peak current after repeated scans occurs because of polymer adsorption onto the electrode surface, which causes a sensitivity decrease in the electrode, as emphasized above. Similarly, as seen in the cyclic voltammogram of BDTCO-co-Py, it has one oxidation peak at 0.49 V with one reduction peak at -0.13 V. According to the electrochemical data obtained from measurements, the decreased oxidation potential after repeated scans and increases at the oxidation and reduction peaks, that is an increase in peak intensity for the repeated scans are evidence of electropolymerization [30]. The experimental conditions to perform the electrocopolymerization reactions are chosen 20 as cycle number and 0.25 V/s as the scan rate, respectively, for all the measurements.

3.3. Spectroelectrochemical properties

The obtained co- and homopolymer films are different colors on the electrode surface (see Fig. 5). The homopolymer P(BDTCO) is a straw colored; BDTCO-co-Th is a fawn colored; BDTCO-co-EDOT is a dark blue colored; BDTCO-co-Py is a brown colored at the neutral states. In order to investigate colors of the polymers and the spectral changes in the range of different potentials at oxidation and reduction states are spectroelectrochemical method, that is,



Fig. 4. Cyclic voltammograms for repeated scans of P(BDTCO), BDTCO-co-Th, BDTCO-co-EDOT and BDTCO-co-Py (scan rate: 0.25 V/s, cycle numbers: 20).

examining changes in the optical properties of a polymer on ITO upon applying a potential. It also provides information about the properties of the conjugated polymer, such as the band gap (E_g) and inter-gap states that appear upon doping. Spectroelectrochemical measurements are conducted at different potentials for each polymer in a 0.1 M



Fig. 5. Optoelectrochemical spectra of P(BDTCO), BDTCO-co-Th, BDTCO-co-EDOT and BDTCO-co-Py in the presence of 0.1 M LiClO₄ in AN.

AN/LiClO₄ solution. Fig. 5 shows the changes in the absorption spectra of P(BDTCO), BDTCO-co-Th, BDTCO-co-EDOT and BDTCO-co-Py at various applied potentials. As the copolymer devices oxidized, the intensities of their π - π^* transitions decreased, and their charge carrier bands at approximately 800 and 900 nm increased because of polaron formation [31]. Therefore, the Th, Py and EDOT copolymers of BDTCO show important changes in their maximum wavelengths. When the potential is applied in the range of 0 and +1.8 V, any changes are not observed in the absorption spectrum of P(BDTCO), but there is only a minor change at approximately 800–900 nm, which comes from polaron formation, as emphasized above. Resultantly, when different potentials are applied to P(BDTCO), its absorbance does not increase; however, this polymer is easily electropolymerizable (see Fig. 4). Moreover, the copolymers of Th, Py and EDOT with BDTCO have remarkably changes in their absorption spectra. For example, when scanned from 0 to +1.8 V, BDTCO-co-Th exhibits gradually an increase in the range of 600-1000 nm. On the other hand, it is seen that the absorption peak intensity decreases a minor reducing at around 400 nm. As seen in the absorption spectrum of BDTCO-co-EDOT, it can be said that the spectral changes are available at two different regions. Similar to BDTCO-co-Th, when scanned from 0 to +1.6 V, increasing the degree of oxidation in BDTCOco-EDOT gradually decreases the absorbance intensity at 550 nm, and simultaneously, shifts this band to longer wavelengths (hypsochromic shift), which corresponds to the presence of positive carriers and the formation of fully doped polymeric chains. As the doping level increased, the sub-gap absorption grew at the expense of the $\pi - \pi^*$ transition [32]. The reduced form of BDTCO-co-EDOT possesses an absorption maximum at 580 nm, which corresponds to an intense blue color, although the oxidized form of BDTCO-co-EDOT possesses a violet colored. Additionally, thin copolymer films of EDOT are transmissive blue-gray in their oxidized state, and a highly absorbing blue-violet in their reduced state, suggesting its use as a cathodically coloring electrochromic material [28]. According to the optical measurement of BDTCO-co-Py, it can be said that the absorbance peak intensity decreases at 380 nm, and simultaneously, the absorbance peak intensity increases at 550 and 850 nm, when scanned from -0.6 to 1.2 V.

3.4. Electrochromic switching and the stabilities

To conduct the spectroelectrochemical measurements, repeated scans with a cyclic voltammeter coupled to an optical spectroscopy method are performed for various scan cycle numbers. The potential scan range is differently chosen for each polymer. The electrochromic switching graphs of the polymers are given in Fig. 6. The measurements are performed using a single wavelength with obviously changing absorption intensity for BDTCO-co-EDOT and P(BDTCO) and also, two wavelengths are used for



Fig. 6. Electrochromic switching of the optical absorbances of BDTCO-co-Py at 370 and 900 nm, BDTCO-co-EDOT at 580 nm, and P(BDTCO) at 700 nm in the presence of 0.1 M LiClO₄ in AN.

BDTCO-co-Py. A scan rate of 0.05 V/s is chosen. During the switching experiment, the λ_{max} values are chosen as 370 and 900, 580 nm and 700 nm for BDTCO-co-Py, BDTCOco-EDOT and P(BDTCO), respectively. The polymer films are deposited onto the ITO-coated glass slides under constant potential conditions, as mentioned above, and their absorbances are monitored at λ_{max} while switching between potentials. As shown in Fig. 6, during the repeated potential scans, the absorption intensity of BDTCO-co-Py is clearly stable between -0.6 V and 1.2 V at 370 and 900 nm for two wavelengths. The response time for BDTCO-co-Py from the neutral (-0.6 V) to the oxidized (1.2 V) states is found to be 25 s at 370 nm and 24 s at 900 nm, respectively. BDTCO-co-EDOT also has good absorption recoveries at the applied potentials, which indicates the percent transmittance (ΔT %) at 580 nm. The stability of the redox states during the scans is the most property for an electro-active polymer to be useful in constructing new electrochromic devices [33-37]. The response time for BDTCO-co-EDOT from the neutral (-1.0 V) to the oxidized (1.6 V) state is found to be 27 s at 580 nm. The ability of a material to exhibit a noteworthy color change is important for electrochromic applications. The electrochemically synthesized polymers on ITO-glass have brown colors in the neutral states and also, both blue and green colors in the oxidized states. As seen in Fig. 5, the response time for P(BDTCO) from the neutral (0.0 V) to the oxidized (1.8 V) states is found to be 25 s at 700 nm. During the switching process, the percent transmittance (T%)is recorded using a UV-Vis spectrophotometer. The optical contrast (ΔT %) was measured as the difference between the T% values recorded for the neutral and oxidized polymer films and found to be 14% at 370 nm and 17% at 900 nm for BDTCO-co-Py, 44% at 580 nm for BDTCO-co-EDOT and 20% at 700 nm for P(BDTCO). The electrochromic switching measurement of BDTCO-co-Th could not be performed due to its film is not successfully coated onto ITO; however, this polymer is easily electropolymerizable and the optical changes can be seen in its spectrum according as variable potential (see Figs. 4 and 5). As a result of their aliphatic-substituted molecular structures, the monomer and polymer chains can be further separated from each other to diminish the effects of aggregation. Therefore, the dopant ions can move more freely into and out of the space between the polymer chains in the electrochromic material during redox switching. In addition, Reynolds and Sankaran found that alkyl - substituted polymers of EDOT (PEDOT-C8 and PEDOT-C14) exhibited improved electrochromic performances relative to unsubstituted PEDOT. They reported that PEDOT-C14 in the oxidized film was 60% transmissive, whereas the reduced film was <5% transmissive ($\Delta T\%$ = 55%) [28]. Therefore, the transmittances of the polymeric structures can be low because of the effects of aliphatic groups.

Fig. 7 presents the changes in the anodic and cathodic peak currents as a function of the potential. The scan rate



Fig. 7. Cyclic voltammograms of P(BDTCO) and BDTCO-co-EDOT as a function of repeated scans 0.05 V/s after 14 cycles for P(BDTCO) and BDTCO-co-EDOT.

is chosen as 0.05 V/s. The polymers show only a slight decrease in electroactivity accompanied by unperturbed color change after 14 cycles for P(BDTCO) and BDTCO-co-EDOT. This result reveals that the synthesized copolymers have reasonable environmental and redox stability [18]. Therefore, the polymers can be operated with different applied potentials for future electrochromic applications.

3.5. Thermal stability

The thermal degradation data (TGA, DTG and DTA) for the compounds are summarized in Table 1, TG curves for the compounds and DSC curve of P-BDTCO are shown in Fig. 8a and b, respectively. According to TG and DTG results, the compounds have different degradation steps. Additionally, the initial degradation temperatures (T_{on}) of the compounds are at around 160 °C, except BDTCO-co-EDOT, which has quite high the initial degradation temperature. This result shows that it is thermally stable. Moreover, temperature values corresponding to weight losses of 20% and 50% are given in Table 1 for each compound, respectively. The char from BDTCO, P-BDTCO, BDTCO-co-Th and BDTCO-co-EDOT is 27.00%, 48.00%, 6.50% and 4.00%, respectively, at 1000 °C. According to these results, the polymer synthesized with FeCl3 has higher carbine residue amount than those of the others. T_{max} values are clearly determined from the DTG curves, and also DTA

Table 1					
Thermal	degradation	values	of th	e com	pounds.

curves indicate that endothermic and exothermic peak for BDTCO at 176 and 837 °C, respectively. At the same time, losses of the solvent occur as 1.29% for BDTCO, 4.89% for P-BDTCO, 8.02% for BDTCO-co-Th and 3.59% for BDTCO-co-EDOT at the range of 20 and 120 °C. DSC analysis of P-BDTCO is performed (see Fig. 8b). The glass transition temperature (T_g) of the polymer is also calculated from its DSC curve and it is found as 132 °C. Also, the change of the specific heat (Δ Cp) during the glass transition is calculated, and found as 3.124×10^{-3} J/g °C. The calculated region is shown as insert figure of Fig. 8b by enlarging, and therefore this peak can be clearly seen. Resultantly, due to the synthesized compounds have high thermal stabilities; they can be promising candidates for aerospace applications.

3.6. Conductivity measurements

The conductivity measurements of the polymers are performed via the four-probe technique at room temperature. While the conductivities of electrochemically prepared polymer films are measured on the electrode surface, the conductivity measurement of P-BDTCO is measured on its pellet at solid state. When the polymer films coated on ITO/glass are exposed to iodine vapor, no structural changes from iodine complexation are observed for the polymers, and their conductivities are, therefore, stable

Compounds	TGA (°C)				DTA (°C)			
	$T_{\rm on}^{\rm a}$	$T_{\rm max}^{\ \ b}$	T ₂₀ , ^c	$T_{50},^{d}$	% Char at 1000 °C	Losses of solvent,% 20-120 °C	Exo	Endo
BDTCO	158	171, 457, 685, 844	304	875	27.00	1.29	837	176
P-BDTCO	163	260, 784	372	819	48.00	4.89	-	-
BDTCO-co-Th	165	277, 696, 930	274	553	6.50	8.02	-	-
BDTCO-co-EDOT	247	334, 467	273	348	4.00	3.59	-	-

^a The onset temperature.

^b Temperature of the peak maxima.

^c Temperature corresponding to 20% weight loss.

^d Temperature corresponding to 50% weight loss.





(see Table 2). But, increasing conductivity of P-BDTCO is obtained via iodine doping and the pellet of P-BDTCO is exposed to iodine vapor during 5 days. As a result, its initial conductivity or conductivity at the undoped state is found as 3×10^{-9} S cm⁻¹. After the doping reaction for 120 h with iodine vapor the conductivity of P-BDTCO nearly increases as 667 times of the initial conductivity (up to 2×10^{-6} S cm⁻¹). Being low of its initial conductivity value is related to the aliphatic groups. This decrease is assumed to be caused by the aliphatic groups which substituted on

Table 2	
Conductivities of the polymers.	
Compounds	

Compounds	Conductivity (S cm ⁻¹)
P-BDTCO S	3.00×10^{-9} (undoped state) 2.00 × 10 ⁻⁶ (doped state)
BDTCO-co-Th	4.50×10^{-5}
BDTCO-co-Py	$1.60 imes 10^{-5}$
BDTCO-co-EDOT	$2.30 imes 10^{-4}$



Scheme 4. Possible complex form of P-BDTCO with I_3^- molecule.



Fig. 9. SEM photographs of BDTCO with (a) 50 μm, (b) 10 μm, (c) 5 μm particle magnifications and P-BDTCO with (d) 50 μm, (e) 10 μm and (f) 5 μm particle magnifications, respectively.

the carbazole nitrogen. Length of these aliphatic groups affect to intermolecular electron transfer. Also, these aliphatic groups hinder the coordination of I_3^- with carbazole nitrogen, because of the steric effect exerted by them. Since nitrogen is a very electronegative element and is capable of coordinating with the I_3^- , Diaz et al. suggested a conductivity mechanism when doped with iodine [38]. Furthermore; it is believed that iodine doping occurs not only on the carbazole nitrogen atoms but also on the thiophene rings. Similarly, sulfur in the thiophene rings is a very electronegative element and is capable of coordinating with the I_3^- , as emphasized above. The conductivity at doped state is high because of coordinating of thiophene rings with the I_3^- molecule [39]. The conductivity mechanism over the polymer backbone can be proposed as Scheme 4.

3.7. Surface morphology

Morphological properties of BDTCO and P-BDTCO are obtained by scanning electron microscopy (SEM) technique. SEM photographs of powder forms are given in Fig. 9 at different magnifications. According to the SEM images, the surface of BDTCO has different sized unhomogenous particles with sharp edges. These sharp edges are probably because of the aliphatic groups in the monomer structure. As seen in Fig. 9c, SEM photograph of BDTCO has vertically platy layers. Also, SEM photographs of the polymer (P-BDTCO) synthesized with FeCl₃ are given in Fig. 9d–f, respectively, at different magnifications. As investigated its SEM images, it can be seen that P-BDTCO is an agglomerate form (see Fig. 9d). Fig. 9f has a collected material surface like collapsing of dried foliages. Moreover, when compared with BDTCO, P-BDTCO is different from it at the same magnifications.

4. Conclusion

According to the spectroelectrochemical measurements, the synthesized copolymers exhibited the electrochromic properties, can be tunable to different colors like straw and violet colors. Spectroelectrochemical analysis of P(BDTCO) was performed at different potentials but no changes in its optical absorbance was observed; however, this material was easily electropolymerizable and also, it had fairly well film stability. Conductivity measurements demonstrated that these polymers were semi-conducting. This result can be explained by the presence of the aliphatic groups in the polymer structures, which decreases conductivity. In addition, increased conductivity of P-BDTCO and the maximal conductivity for P-BDTCO were obtained via iodine doping when exposed to iodine vapor. As a result, P-BDTCO could also be useful materials in electronic or optoelectronic studies by doping with iodine for a long time. The resultant data showed that the electrochemically synthesized copolymers could be used in electrochromic devices.

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