



Novel Fluorene and Pyrrole Comprising Copolymers: Effect of Copolymer Feed Ratio on Electrochromic and Electrochemical Properties

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Abstract. Herein, synthesis of two homopolymers namely, poly-2,2'-(9,9-dioctyl-9h-fluorene-2,7-diyl)bisthiophene (PBT), poly-pyrrole-3-carboxylic acid (PP3CA) and fluorene and pyrrole comprising five novel copolymers (CoP1, CoP2, CoP3, CoP4, CoP5) were electrochemically synthesized. Each electrolytic solution was prepared with different monomer feed ratios to investigate the effect of comonomer ratio on electrochromic and electrochemical properties. After synthesis, homopolymers and copolymers were compared in terms of their electrochemical, spectroelectrochemical and colorimetry properties. The number of studies on electrochromic characterization of pristine P3CA group was limited in literature, hence in this study P3CA was electrochemically inserted into the polymer chain via copolymerization. CoP1 with 1:1 (BT: P3CA) monomer feed ratio exhibited the lower optical band gap and red shifted neutral state absorption compared to PP3CA, additionally light yellow color of PP3CA turned out to be multichromic for CoP1 with the insertion of BT unit via electrocopolymerization.

Keywords: Fluorene, pyrrole, copolymerization, electrochromism

Fluoren ve Pirol İçeren Kopolimerler: Kopolimer Besleme Oranının Elektrokimyasal ve Elektrokromik Özellikler Üzerine Etkisi

Özet. Bu çalışmada, poli-2,2'-(9,9-dioktil-9h-fluoren-2,7-diyl)bistiyofen (PBT) ve poli-pirol-3-karboksilik asit (PP3CA) olarak adlandırılan iki polimerin ve ayrıca fluoren ve pirol gruplarını içeren 5 tane yeni kopolimerin (CoP1, CoP2, CoP3, CoP4, CoP5) sentezi elektrokimyasal yöntemlerle gerçekleştirilmiştir. Kopolimer çözeltileri BT ve P3CA monomerlerinin farklı besleme oranlarında karışımı ile hazırlanarak, monomer besleme oranının kopolimerin elektrokimyasal ve elektrokromik özellikleri üzerine etkisi incelenmiştir. Elektrokimyasal polimer sentezlerinin ardından tüm homopolimer ve kopolimerlerin elektrokimyasal, elektrokromik ve kolorimetrik çalışmaları yapılmıştır. Literatürde P3CA monomerinin elektrokromik çalışmalarının az olması nedeniyle, bu yapı BT monomeri ile beraber kopolimer zincirine katılmıştır. Kopolimerler içinde, 1:1 (BT: P3CA) monomer besleme oranı ile hazırlanan CoP1 kopolimeri, PP3CA homopolimeri ile kıyaslandığında daha düşük bant aralığı ve multikromik özellikler göstermiştir.

Anahtar Kelimeler: Fluoren, pirol, kopolimerizasyon, elektrokromizm

1. INTRODUCTION

Electrochromic polymers are types of organic materials which can change their colors with applied potential have gained a great attention in recent years especially for many display and optoelectronic applications. In addition, electrochromism could be achieved with very low potential difference which strongly depends on the

structure of the polymers. Although many inorganic molecules and organic compounds were widely used as electrochromic materials, organic conducting polymers (CPs) have drawn great interest due to their superior properties, such as relatively low cost, easy structural modification via chemical synthesis, color tunability, fast switching

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time and high coloration efficiency [1-5]. As a result of these attractive properties, CPs have been used not only for electrochromic applications but also in wide range of technological areas such as organic photovoltaics (OPVs), organic light emitting diodes (OLEDs), field effect transistors (FETs), sensors and super capacitors (SCs) over the last two decades [6-10]. In order to use the CPs for the abovementioned applications, the value of the band gap and corresponding HOMO-LUMO energy levels are crucial factors. In recent years, the synthesis of multipurpose smart polymers with enhanced electronic and optical properties are the main purpose of the researchers in this field and this purpose can be achieved with controlling the structural alterations [11].

In literature, bond length alternation, planarity, interchain alternation, resonance effect, diverse pendant groups and donor-acceptor theory were well known strategies for controlling electronic and optoelectronic features of CPs, however donor-acceptor approach is considered as the most proper one to design CPs with unique and enhanced physicochemical properties. [12-14] Combination of different donor and acceptor units in the polymer backbone yields multipurpose copolymers with enhanced electrochemical and optical properties such as switching time, neutral and oxidized state colors and coloration efficiency. Another popular strategy for structural modification is copolymerization of different monomers. Via copolymerization, physicochemical behaviors could be altered easily and the units which can not be polymerized could be inserted into the polymer backbone [15,16]. Copolymerization can be performed via chemically or electrochemically in the presence of at least two comonomers with different monomer feed ratios. When compared to chemical copolymerization, electrochemical one has some certain advantages such as simplicity, easy and fast polymer synthesis and synthesis of well adhered copolymer film on an electrode surface. Additionally, after electrocopolymerization the electro-optical behaviors of the resulting copolymer films could be investigated with the same electrode easily [17].

In literature, different type of units such as; benzothiadiazole (BTd), quinoxaline (Qx), benzotriazole (BTz), carbazole (Cz), bithiophene, propylenedioxythiophene (ProDOT), fluorene and 3,4 ethylene dioxythiophene (EDOT) were widely used for electrochemical copolymerization and electrochromic applications. [18-20] Among a

great deal of electroactive polymers, polyfluorenes aroused interest as a blue light emitter with their high thermal and chemical stability and photostability both in solution and solid state. [21] However, some crucial drawbacks such as; poor solubility, aggregation in the solid state and high energy barrier for hole injection limited the possible application fields of PF. Copolymerization of fluorene with different comonomers resulted multipurpose functional copolymers with enlarged application fields [22,23]. Another interesting and popular comonomer unit is pyrrole (Py) due to some certain structural advantages such as; high electrical conductivity, easy preparation, chemical stability, structural versatility and biocompatibility. These unique properties increased the applicability of Py comprising polymers in different fields especially electrochemical and biological applications [24-26].

In the light of these, the main purpose of this study is to combine the promising properties of fluorene and Py monomers via electrochemical copolymerization technique. Herein, syntheses of two homopolymers (PBT and PP3CA) and design of five novel copolymers (CoP1, CoP2, CoP3, CoP4, CoP5) of BT and P3CA in different monomer feed ratios were performed. The electrochemical, spectroelectrochemical and colorimetric properties of resulting homopolymers and copolymers were explored and reported. Finally, the effect of copolymer feed ratio on electrochromic and electrochemical properties were also discussed.

2. EXPERIMENTAL

2.1. Materials and Equipments

2,2'-(9,9-Dioctyl-9h-Fluorene-2,7-Diyl)bisthiophene (BT), pyrrole-3-carboxylic (P3CA) (Fig. 1) are commercially available monomers and purchased from Sigma- Aldrich Chemical Co. Ltd. and used without any further purification. GAMRY 600 potentiostat/galvanostat was used for cyclic voltammetry studies and UV-Vis spectra characterizations were monitored at ambient temperature and conditions via Varian Carry 5000 UV-Vis spectrophotometer.

electrolyte/solvent system was used for electrochemical copolymerization. As seen in Figure 3 and Figure 4, an increase in anodic and cathodic current densities were observed for all copolymers which prove the continuous copolymerization and the deposition of copolymer films on ITO coated glass slides. Then single scan CVs were recorded for all copolymers in a monomer free medium. From single scan CVs, oxidation potentials were calculated as 0.79/1.05V (CoP1), 0.53/0.98 V (CoP2), 0.83 V (CoP3), 0.76/1.05 V (CoP4) and 0.80/1.10 V (CoP5). Besides, corresponding HOMO energy levels were calculated from Eqn 1 and reported in Table 1 as -5.31eV(CoP1), -5.04 eV(CoP2), -5.29 eV(CoP3), -5.60 eV(CoP4) and -5.61eV(CoP5), respectively. As seen, two oxidation potentials at around 0.75 V and 1.00 V were observed for CoP1, CoP2, CoP4 and CoP5 which prove the successful insertion of comonomer units (BT and P3CA) into the copolymer chains. CVs of all copolymers (CoP1, CoP2, CoP3, CoP4 and CoP5) for both electrochemical copolymerizations and single scans recorded in a monomer free medium were reported in Figure 3 and Figure 4.

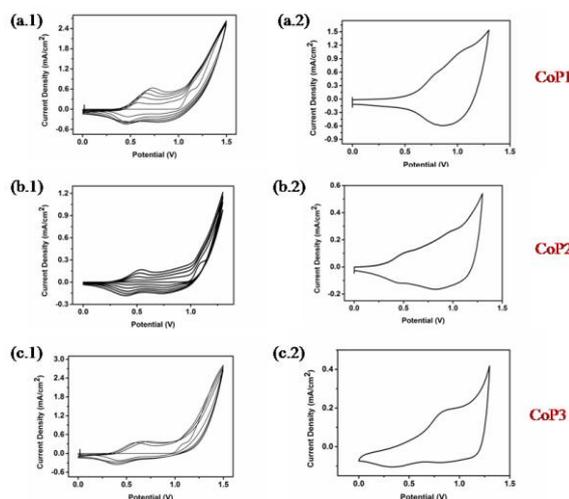


Figure 3. Cyclic voltammograms of (a.1) CoP1 (b.1) CoP2 (c.1) CoP3 during the electropolymerization on ITO-coated glass electrode and (a.2, b.2, c.2) single scan cyclic voltammograms of the resulting copolymers.

Cyclic voltammograms of CoP1, CoP2 and CoP3 during the electropolymerization and single scan CVs of the resulting copolymers were depicted in Figure 3. As seen, CoP1 with 1:1 (BT:P3CA) comonomer feed ratio exhibited two oxidation peaks at 0.79 V and 1.05 V with higher current density compared to those of CoP2 and CoP3. When P3CA ratio was increased into the copolymer chain, electroactivity of CVs depleted with lower current density as seen in single scan

CVs which can be dedicated to the poor electroactive character of P3CA.

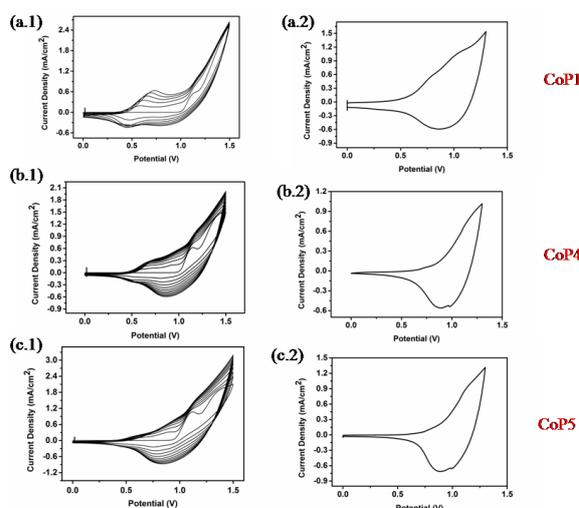


Figure 4. Cyclic voltammograms of (a.1) CoP1 (b.1) CoP4 (c.1) CoP5 during the electropolymerization and (a.2, b.2, c.2) single scan cyclic voltammograms of the resulting copolymers.

Cyclic voltammograms of CoP1, CoP4 and CoP5 during the electropolymerization and single scan cyclic voltammograms of the resulting copolymers were illustrated in Figure 4. As seen, the increasing amount of BT unit into copolymer chain affected electrochemical behaviors positively with increasing current density and electroactivity. Besides, as mentioned before copolymers exhibited two oxidation potentials at around 0.75 V and 1.00 V arising from P3CA and BT comonomers, respectively. As BT comonomer feed ratio was increased from CoP1 to CoP5, the intensity of the latter one increased significantly which proves the increasing number of BT unit into the copolymer chain. (Figure 4)

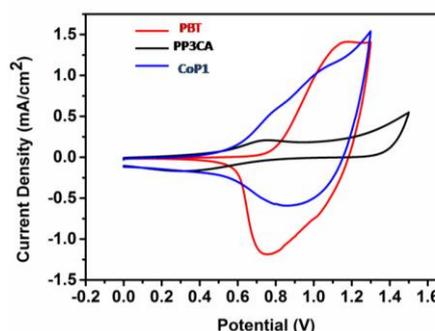


Figure 5. Single scan cyclic voltammograms for PBT, PP3CA and CoP1.

In order to investigate the effect of different comonomer units (P3CA and BT) on electrochemical behaviors, single scan CVs for PBT, PP3CA and CoP1 were recorded and reported in Figure 5. As mentioned before, BT unit was

inserted into the copolymer structure in order to improve the electrochemical behaviors and as seen in Figure 5, CoP1 exhibited higher current density and higher electroactivity compared to those of

PP3CA which enlarge the application fields of P3CA comprising copolymers

Table 1. Summary of electrochemical and spectroelectrochemical properties of PBT, PP3CA and corresponding copolymers

	Monomer feed ratio (BT: P3CA)	$E^{\text{mon}_{\text{ox}}}$ (V)	$E_{\text{p-doping}}$ (V)	$E^{\text{ox}_{\text{onset}}}$ (V)	HOMO (eV)	λ_{max} (nm)	$\lambda_{\text{max}_{\text{onset}}}$ (nm)	E_{g}^{op} (eV)
PBT	1:0	1.18	1.00	0.79	-5.54	430	540	2.29
PP3CA	0:1	1.13	0.75	0.44	-5.19	397	600	2.07
CoP1	1:1	-	0.79/1.05	0.56	-5.31	412	650	1.91
CoP2	1:3	-	0.53/0.98	0.29	-5.04	420	560	2.21
CoP3	1:5	-	0.83	0.54	-5.29	400	611	2.03
CoP4	3:1	-	0.76/1.05	0.85	-5.60	419	584	2.12
CoP5	5:1	-	0.80/1.10	0.86	-5.61	424	628	1.98

3.2. Spectroscopic Characterization

After electrochemical copolymerization and characterizations, the spectral behaviors were recorded with UV-VIS spectrophotometer in order to investigate the electronic transitions and changes in optical properties upon applied potential. The effect of the changing monomer feed ratio on the optoelectronic properties of the fluorene and pyrrole comprising electroactive copolymers were examined by spectroelectrochemical studies. In addition, from these studies some crucial parameters such as; maximum absorption wavelengths (λ_{max}), optical band gap and polaron/bipolaron bands were determined.

Before stepwise oxidation, electrochemically synthesized copolymer films were reduced to neutral states by applying a constant potential to remove any trapped charge and dopant ions. Then, the neutral films were oxidized stepwise and electronic absorption spectra were recorded in a monomer free 0.1 M $\text{LiClO}_4\text{-NaClO}_4$ /ACN solution.

As seen in Figure 6 and Figure 7, the maximum absorption wavelengths (λ_{max}) for homopolymers and copolymers were centered at 430 nm (PBT), 397 nm (PP3CA), 412 nm (CoP1), 420 nm (CoP2), 400 nm (CoP3), 419 nm (CoP4), 424 nm (CoP5). As mentioned before the P3CA homopolymer exhibited poor electrochemical behaviors, in addition the neutral state absorption of P3CA was centered in the UV region which limit the

application fields. In this study, insertion of fluorene derivatives into the copolymer structure with different monomer feed ratios enhanced the electrochromic and spectroelectrochemical behaviors. As seen in Figure 6, while P3CA homopolymer showed light yellow color both in the neutral and oxidized states, CoP1 with 1:1 (BT: P3CA) monomer feed ratio exhibited multichromic behavior. While homopolymers showed λ_{max} values centered at 430 nm (PBT) and 397 nm (PP3CA), all copolymers exhibited λ_{max} values between those values, additionally as the P3CA feed ratio was increased in the copolymer structure an obvious red shift was observed.

During spectroelectrochemical measurements, new absorption bands were observed at around 700 nm for both homopolymers and copolymers due to the formation of charge carriers named as polarons (radical cations) on the polymer backbone. During stepwise oxidation, the intensity of the polarons increased significantly, meanwhile the intensity of the neutral state absorptions gradually diminished.

Another important parameter of electroactive polymers for variety of applications is the optical band gap value which can be calculated from neutral state absorption. Herein, optical band gaps of both homopolymers and copolymers were determined from the onset of their lowest energy $\pi\text{-}\pi^*$ transitions as 2.29 eV (PBT), 2.07 eV (PP3CA), 1.91 eV (CoP1), 2.21 eV (CoP2), 2.03 eV (CoP3), 2.12 eV (CoP4), 1.98 eV (CoP5), respectively. When homopolymers and copolymers were compared in terms of optical characters, while PBT

exhibited the highest optical band gap due to its UV-region covered absorption, CoP1 with 1:1 (BT: P3CA) monomer feed ratio showed the lowest optical band gap due to its red shifted absorption.

and green and 'b' represents the color between yellow and blue in the colorimetric measurements. The corresponding L, a, b results for both homopolymers and copolymers were reported in Table 2. As mentioned before, the light yellow color of P3CA homopolymer observed both in the neutral and oxidized states were changed to multichromic behavior via insertion of BT unit into the copolymer chain with 1:1 (BT: P3CA) monomer feed ratio. Additionally, lower optical band gap and red shifted neutral state absorption were investigated for CoP1. In this study P3CA group was electrochemically inserted into the copolymer chain with copolymerization technique, and as a separate study the P3CA comprising copolymers will be used for biosensor applications in our research group.

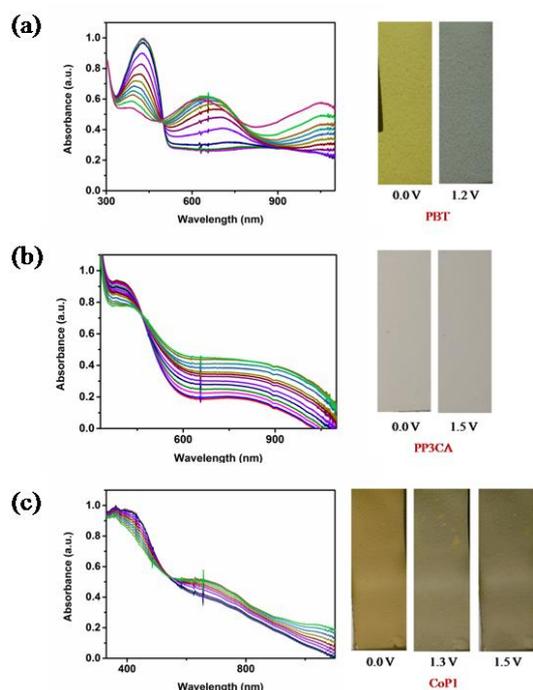


Figure 6. UV-Vis spectra of (a) PBT (b) PP3CA and (c) CoP1 during a slow oxidation process in a 0.1 M LiClO₄-NaClO₄ /ACN monomer-free solution with corresponding colors in the neutral and oxidized states.

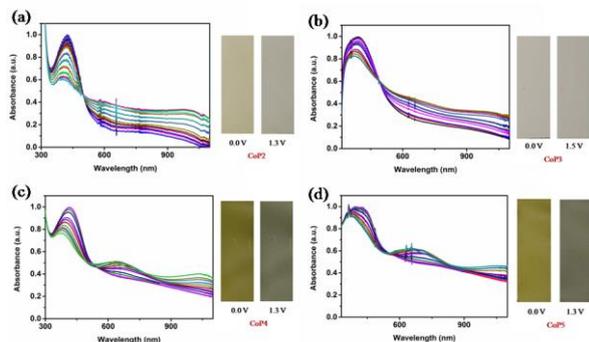
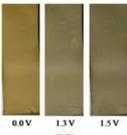


Figure 7. UV-Vis spectra of (a) CoP2 (b) CoP3 (c) CoP4 and (d) CoP5 during stepwise oxidation in a 0.1 M LiClO₄-NaClO₄ /ACN monomer-free solution with corresponding colors in the neutral and oxidized states.

Finally, colorimetric studies were performed in order to report the colors of all copolymers both in the neutral and oxidized states. For colorimetric studies photographs of the polymers films were recorded and reported in Table 2 with the corresponding L, a, b values according to CIE (Commission Internationale de l'Eclairage) coordinates. CIE coordinates were widely used to report the colors of materials in a more scientific way. While 'L' represents the brightness of the color, 'a' represents the color between red/magenta

Table 2. Colorimetric measurements of the homopolymers and copolymers.

Polymer	Applied potential	L	a	b	
PBT	0.0 V	66	-8	48	
	1.2 V	55	-5	7	
PP3CA	0.0 V	71	1	6	
	1.5 V	69	0	6	
CoP1	0.0 V	52	4	39	
	1.3 V	41	-1	23	
	1.5 V	49	1	21	
CoP2	0.0 V	72	-2	16	
	1.3 V	68	-1	8	
CoP3	0.0 V	72	2	6	
	1.5 V	69	0	5	
CoP4	0.0 V	42	-4	38	
	1.3 V	44	-3	15	
CoP5	0.0 V	54	-3	39	
	1.3 V	47	-2	13	

4. CONCLUSION

Fluorene and pyrrole bearing electrochromic homopolymers (PBT and PP3CA) and novel copolymers (CoP1, CoP2, CoP3, CoP4, CoP5) with different monomer feed ratios were synthesized via electrochemical technique. After successive electropolymerization, the

electrochemical, spectroelectrochemical and colorimetric properties were investigated for all polymers. All copolymers exhibited different electrochemical and optical properties when compared to their homopolymers. While homopolymers PBT and PP3CA exhibited λ_{\max} values centered at 430 nm and 397 nm, all copolymers exhibited λ_{\max} values between those values. In addition, in terms of optical behaviors as

the P3CA feed ratio was increased in the copolymer structure the obvious red shift was observed on spectroelectrochemical characterizations. While PBT showed yellow and green colors in the neutral and oxidized states, the light yellow color was observed for P3CA in both states. However multichromic behavior was explored for CoP1 via insertion of BT unit into the copolymer chain with 1:1 (BT: P3CA) monomer feed ratio. Additionally, lower optical band gap and red shifted neutral state absorption were investigated for CoP1 compared with pristine PP3CA. Finally, in this study P3CA group was electrochemically inserted into the copolymer chain successfully and electrochromic characters were investigated in detail, in future the P3CA bearing copolymers will be used for biosensor applications in our research group.

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