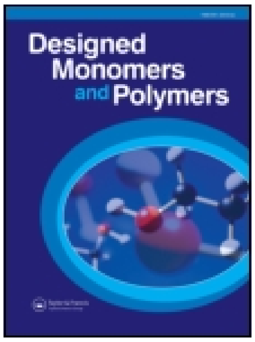

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The effect of the monomer feed ratio and applied potential on copolymerization: investigation of the copolymer formation of ferrocene-functionalized metallopolymer and EDOT

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ABSTRACT

In this study, we reported synthesis of ferrocene functioned conducting metallopolymer to enhance the understanding of properties of polymers. One of the crucial ways in the electrochromic polymer materials research was tuning color by means of copolymerization and change of polymer backbones and side groups. For this purpose, we synthesized copolymer of 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)amido ferrocenyl dithiophosphonate with EDOT via potentiodynamic electrolysis. Spectral and electrochemical characterizations of the copolymer were investigated. In addition, the spectral properties of the copolymers prepared by different applied potentials and different monomer feed ratio were studied. For the first time, copolymer composition and the monomer reactivity ratios were approximately calculated by using the spectral data.

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Conducting polymers; metallopolymer; copolymerization; spectroelectrochemistry; feed ratio

1. Introduction

Metallopolymers containing transition metals in their backbone are interesting class of materials and they have been extensively studied in the last years. These metal-containing polymers have distinct physical and electrochemical properties.[1] These properties can be improved by the type of metal in the conjugated organic polymer chain. Thanks to their distinct properties, they have also been used in agricultural, medicinal, and technological field.[2–4] When the metal is incorporated into polymer structure, it achieves unique electrochemical and optical behavior via electron transfers within the organic matrix which would enable to use as optic-based material.[5] One of the ways to prepare new organic conducting metallopolymer is the combination of conductive polymers with dithiophosphonates. Conducting polymers play an important role in the technological areas such as polymer light emitting diodes,[6,7] gas sensors,[8] organic photovoltaic devices,[9] electrochromic devices,[10] organic transistors [11] fuel cells [12,13], and biosensors.[14–16] The combination of inorganic and organic components has made an immense area of new functional materials accessible — the next generation of electronic materials, sensors, electrocatalysis and photoelectronics.[17]

Electrochromism is one of the most investigated properties of conducting polymers. One of the crucial ways in the electrochromic polymer materials research is tuning color by means of copolymerization. The improvement of electrochromic property of polymers with copolymerization is a facility and easy method.[18,19] The properties of the copolymers are determined by the structure and sequence of the repeating units of the monomers.[20,21]

EDOT has been revealed as an appropriate monomer in applications of electrochemical copolymerization due to the low band gap, excellent conductivity, unusual thermal stability, and good electrochemical and electrochromic properties.[22–24]

The chemical structure of a polymer depends on how the monomers distribute along the chain of the macromolecule. This distribution is the direct result of the reactivity of each molecule in the solution. Determination of copolymer composition is an important step to control the physical and chemical properties of the material. The most common mathematical model in copolymerization is based on finding the relationship between copolymer composition and monomer feed composition which is able to find out the ratio of monomer reactivity parameters. The correct estimation of copolymer composition and stability with the monomer reactivity ratio is quite important for the evaluation of the physical chemical properties of copolymers with certain applications.[25] Generally, monomer reactivity ratios are calculated for the copolymers formed by poly-condensation reactions in the literature. Studies of monomer reactivity ratio calculation

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for the conductive polymers are limited.[26] Among most important study is calculation of composition of soluble polythiphone copolymers that obtained via grignard methathesis polymerization reactions.[27,28]

However, estimation of copolymer composition and determination of monomer reactivity ratios are especially difficult for the insoluble conducting polymers.

In this research, we reported the synthesis of ferrocene-functionalized inorganic–organic conducting polymer (SNS-Fc) and its copolymer with EDOT via potentiodynamic and constant potential electrolysis techniques. Spectral and electrochemical properties of the copolymers prepared by different applied potentials and different monomer feed ratio were investigated. For the first time, copolymer composition and the monomer reactivity ratios were approximately calculated by using the spectral data in conducting polymers. Therefore, this study is novel and significant for determination of copolymer reactivity ratios in the conducting polymers.

2. Experimental

2.1. Materials

Thiophene, dichloromethane (DCM), and Aluminum chloride were purchased from Merck. Acetonitrile, toluene, succinyl chloride, hydrochloric acid, sodium bicarbonate, ethanol, p-phenylene diamine, propionic acid, tetrabutylammonium hexafluorophosphat (TBAFP), and 3,4-Ethylenedioxythiophene (EDOT) were bought from Sigma Aldrich.

2.2. Instrumentation

The three electrode system connected to Iviumstat Electrochemical Potentiostat – Galvanostat Device (Netherlands) was used for chronocoulometry and cyclic voltammetry (CV) studies. For spectroelectrochemistry studies, we used Agilent 8453 UV-visible spectrometer coupled with Gamry Reference 600 potentiostat. An NMR spectrum of monomer was recorded by Bruker Ultra Shield Plus 400 MHz NMR spectrophotometer.

2.3. Synthesis 4-(2,5-di (thiophen-2-yl)-1H-pyrrol-1-yl)amido ferrocenyldithiophosphonate

The monomer SNS-Fc was synthesized by similar method in the literature.[13] $[FcP(=S)(\mu\text{-}S)]_2$ (0.21 g, 0.39 mmol) and 4-(2,5-di (thiophen-2-yl)-1H-pyrrol-1yl) aniline (0.25 g, 0.78 mmol) dissolved in toluene (25 mL) and refluxed. The reaction mixture was filtered and the solution was allowed to stand on −18 °C. The resulting yellow–orange crystalline product was filtered and dried under vacuum. SNS-Fc (4-(2,5-di (thiophen-2-yl)-1H-pyrrol-1-yl)amido ferrocenyldithiophosphonate) was synthesized with 60% yield.

2.4. Synthesis of copolymer SNS-Fc with EDOT

EDOT was used as the co-monomer for the synthesis of conducting copolymer P(SNS-Fc-*co*-EDOT), (Scheme 1). A stock solution of 0.01 M SNS-Fc and 0.01 M EDOT were dissolved in 0.05 M TBAFP/DCM electrolyte-solvent system for electrochemical synthesis of copolymer. Copolymer films were prepared electrochemically at the applied potential of 1.5 V. Short notations of A, B, C, D defined the copolymer films obtained from SNS-Fc/EDOT comonomer feed ratios of (4/1), (3/2), (2/3), and (1/4), respectively.

2.5. Scan rate investigations in cyclic voltammetry

P(SNS-Fc-*co*-EDOT) copolymer (1/4 feed ratio) was electrochemically synthesized by applying 1.5 V constant potential on the ITO electrodes. The resulting polymer film was washed by DCM to remove unreacted monomers, and different scan rates in cyclic voltammetry were taken in monomer-free electrolytic solution.

2.6. Spectroelectrochemical properties

For investigation of spectroelectrochemical properties of P(SNS-Fc) and copolymers, a silver wire used as the reference electrode, PT wire used as the counter electrode, and indiumtinoxide (ITO)-coated glass slide used as the working electrode in the cell.

Maximum wavelength (λ_{max}) of copolymers prepared four different monomer feed ratio were measured in TBAFP 0.05 M/DCM solvent system at 1.5 V constant potentials. Copolymer composition was measured by observing λ_{max} differences of copolymers obtained spectroelectrochemical studies. Monomer reactivity ratios and color change of the copolymers were determined. E_g values of P(SNS-Fc), copolymers and PEDOT were measured by absorption spectroscopy of the conjugated polymer films. Since the absorption spectrum reveal information on electronic transition, the onset of absorption is considered as the band gap of semiconductor or conjugated polymers. E_g can be calculated according to the following equation $E_g = 1240/(\lambda_{onset})$ (eV) where the unit of λ_{onset} is nm.

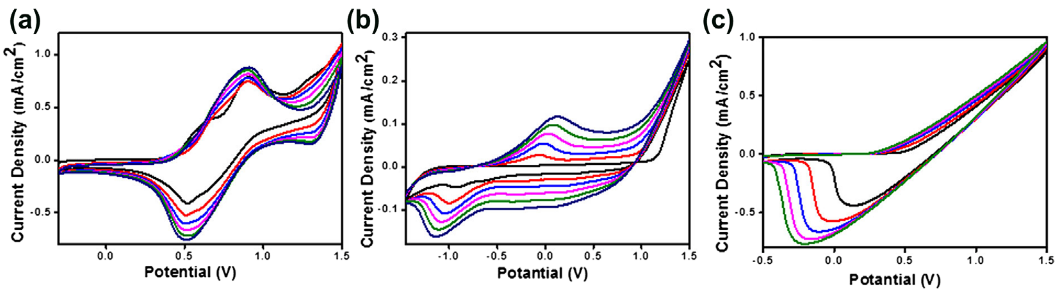


Figure 1. (a) P(SNS-Fc), (b) P(EDOT) and (c) P(SNS-Fc-*co*-EDOT) Cyclic Voltammetry Graphs in 0.05 M TBAFP/DCM electrolyte/solvent couple with 250 mV/s scan rate.

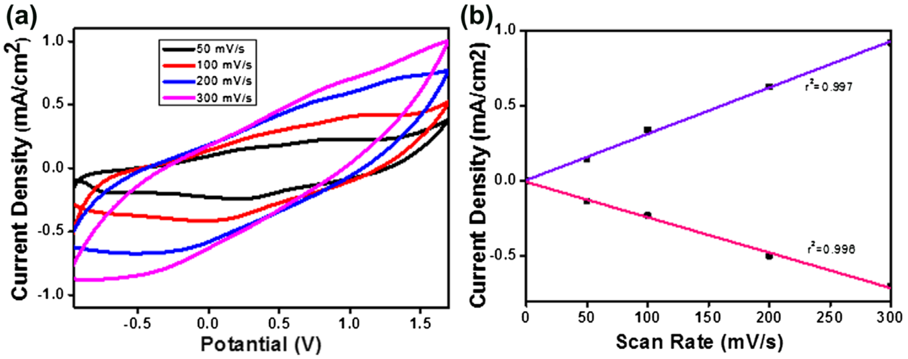


Figure 2. (a) Cyclic voltammetry of P(SNS-Fc-*co*-EDOT), (b) peak current vs. scan rate for P(SNS-Fc-*co*-EDOT).

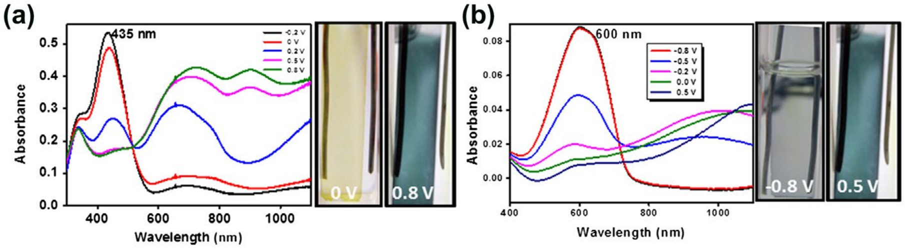


Figure 3. Optoelectrochemical spectra of (a) P(SNS-Fc) and (b) PEDOT.

Table 1. E_g, λ_{max}, f_1 and F_1 values of different monomer feed ratios and Fineman–Ross values for copolymerization at 1.5 V constant potential.

Polymer	Monomer feed ratio	f_1	F_1	λ_{max} (nm)	E_g (eV)	f_i^2/F_1	$f_1(1 - F_1)/F_1$
P(SNS-Fc)	1:0	1.00	1.00	435	2.31	–	–
Copolymer A	4:1	0.80	0.98	437	2.18	0.65	0.016
Copolymer B	3:2	0.60	0.88	454	2.00	0.41	0.081
Copolymer C	2:3	0.40	0.60	503	1.71	0.27	0.26
Copolymer D	1:4	0.20	0.26	560	1.68	0.15	0.57
P(EDOT)	0:1	0	0	600	1.63	–	–

3. Result and discussion

3.1. Copolymerization

The redox behaviors of SNS-Fc, EDOT and SNS-Fc-*co*-EDOT were investigated in an electrolyte solution containing 0.05 M TBAFP/DCM electrolyte/solvent couple with 250 mV/s scan rate by cyclic voltammetry. Firstly, homopolymer (P(SNS-Fc)) and PEDOT were synthesized potentiodynamically via potential swept between −0.5/1.5 V and −1.5/1.5 V, respectively (Scheme 1). There is an increase in the intensity of the current as the number of cycles for P(SNS-Fc) (Figure 1(a)). EDOT was polymerized by cyclic voltammetry between −1.5 and 1.0 V. EDOT polymerization was preceded successfully after each cycle. The

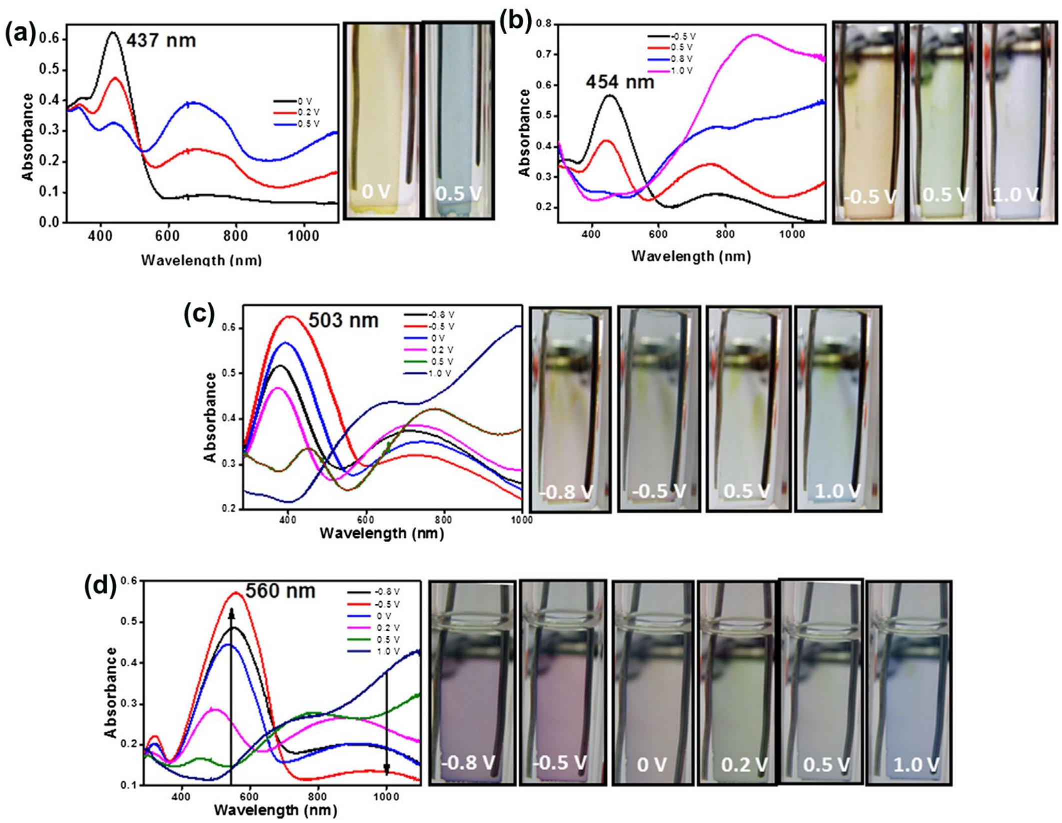


Figure 4. Optoelectrochemical spectra of copolymers synthesized (a) 4:1, (b) 3:2, (c) 2:3, (d) 1:4 SNS-Fc and EDOT momomer feed ratios.

appearance of reversible redox couples after first scan and an increase in the redox couple currents demonstrate the formation of a conjugated polymer on the electrode surface. PEDOT showed one broad redox couple in a monomer-free electrolyte solution (Figure 1(b)). The copolymer CV graph is different in terms of shape and potential values from EDOT and SNS-Fc. These results proved the copolymerization between SNS-Fc and EDOT (Figure 1(c)).

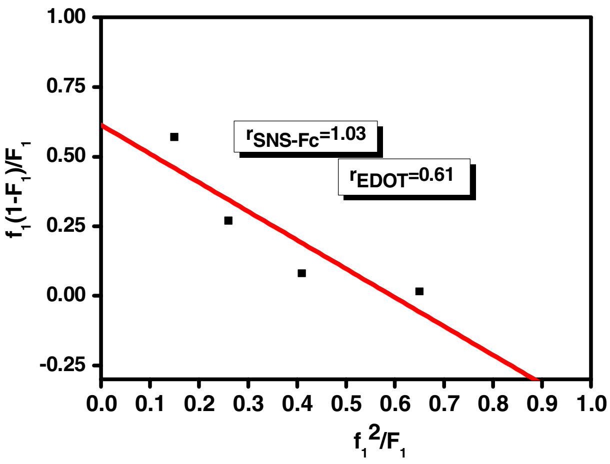


Figure 5. Fineman–Ross plot for copolymerization of SNS-Fc and EDOT.

3.2. Scan rate dependence of P(SNS-Fc-co-EDOT)

P(SNS-Fc-*co*-EDOT) film was characterized by peak currents versus scan rate dependence. Copolymer film was prepared by constant potential and investigated by CV at different scan rates in monomer-free electrolytic solution. Scan rate showed a linear dependence as anodic and cathodic peak currents as shown in (Figure 2). Linearty of the anodic and cathodic peak currents of the voltammetric response with scan rate indicated that both anodic and cathodic charge-transport processes within copolymer films are not diffusion-controlled.

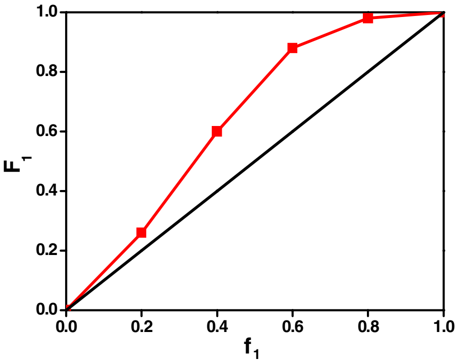


Figure 6. Copolymer composition F_1 against monomer feed ratio f_1 graphs.

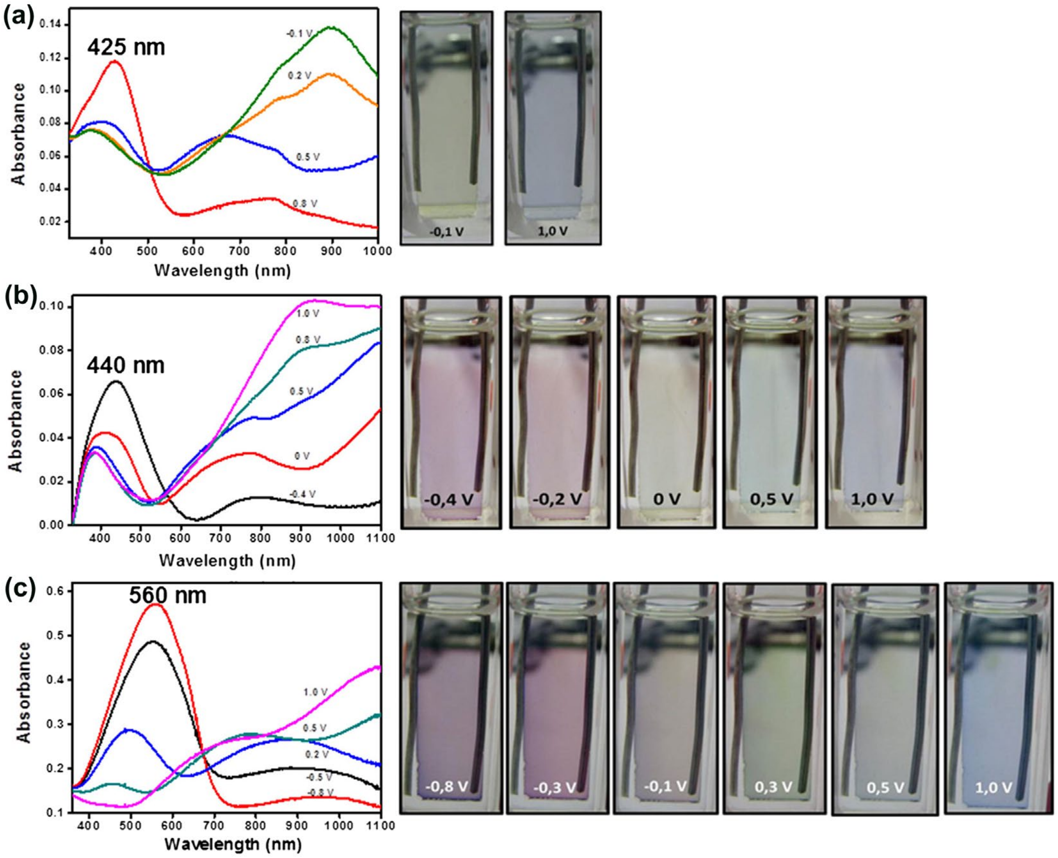


Figure 7. Optoelectrochemical spectra of the copolymers synthesized by different applied potentials (a) 1.0 V, (b) 1.3 V, and (c) 1.5 V.

Table 2. Effect of applied potential on copolymerization.

Polymer	λ_{max}	E_g (eV)
P(SNS-Fc)	435	2.31
Copolymer I (1.0 V)	425	2.26
Copolymer II (1.3 V)	440	2.10
Copolymer III (1.5 V)	560	1.68
P(EDOT)	600	1.63

3.3. Spectroelectrochemical calculation of reactivity ratios and copolymer composition

Spectroelectrochemical properties of P(SNS-Fc), PEDOT, and theirs copolymer films were investigated. The compositions of copolymer were determined by using maximum absorption wavelength values of homopolymer and copolymers. Maximum absorption wavelengths (λ_{max}) of π-π^* transitions for P(SNS-Fc) and PEDOT were found 435 nm and 600 nm respectively, from optoelectrochemical spectra of the polymers (Figure 3a and b). λ_{max} values of copolymers were obtained between that of P(SNS-Fc) and PEDOT (Figure 3).

Concentration of the monomer solutions was prepared according to determined monomer feed ratios. Table 1 shows the comparison of properties of PEDOT, homopolymer, and co-polymers. Maximum wavelengths of the copolymers were between the range of PEDOT and the homopolymer. In addition, band gaps (E_g) of homopolymers and copolymers were calculated. These are all dependent on EDOT how to enter a polymer backbone structure, the conjugation of the polymer, and their effects on the polymer backbone. The band gap energies and absorption maxima of the copolymers were found to be different than the ones for PEDOT and P(SNS-Fc). In addition, the λ_{max} values of the copolymers were red-shifted compared to that of the homopolymer, which is due to increase in conjugation length and the influence of high electron density resulting from the incorporation of EDOT into SNS-Fc units. Therefore, as the amount of EDOT increases in the copolymer, the maximum wavelength of the π–π* transition increases and the electronic band gaps for these copolymers (measured as the onset of the π–π* transition) decrease (Table 1). The spectroelectrochemistry

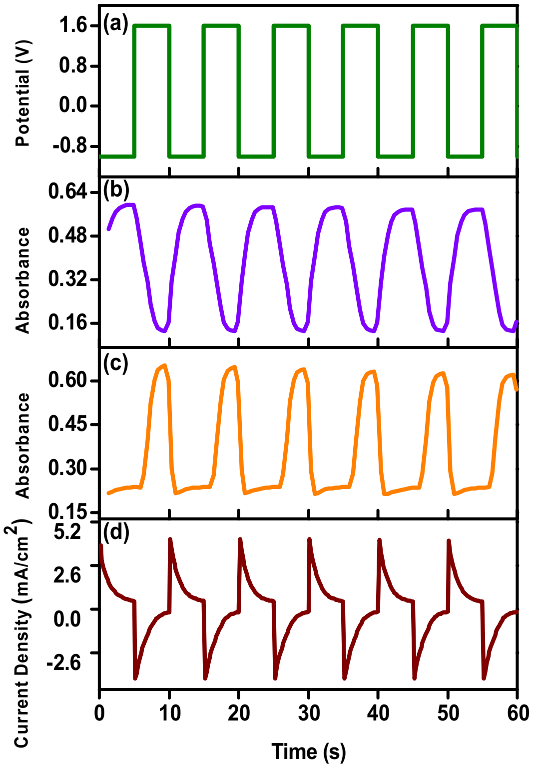
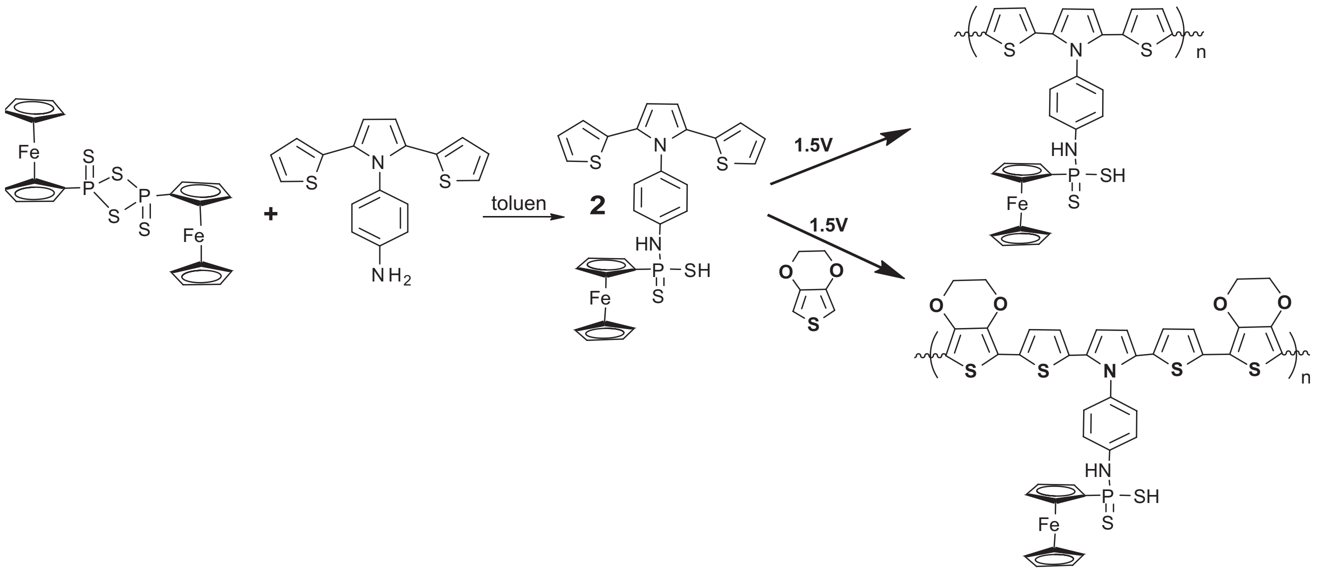


Figure 8. (a) Potential-time, (b) absorbance-time at 1000 nm, (c) absorbance-time at 580 nm, (d) current density-time graphs of P(SNS-Fc-*co*-EDOT).

results demonstrated that as the potential of the polymerization rises, the amount of PEDOT of the copolymer composition rises. As a result, considerable changes in the optical properties of copolymers were obtained. Figure 4 shows spectroelectrochemical spectra of homopolymers and copolymers about different feed ratios and their redox colors. Using a maximum wavelength of the π–π*, electronic transitions corresponding to E_g values (energy band gap) of the copolymers were found (Figure 5).

The product of the monomer reactivity ratios for a given binary copolymerization system is often used to show the sequencing in the resultant copolymerization type and copolymer composition.[29–31] In a monomer pair, the reactivity ratios of unity, a product of the reactivity ratios, and also approximation unity of the monomers are in the same manner incorporated into the growing chain. As a result, this copolymerization is said to be ideal (random). When the product of the reactivity ratios is disparate (i.e. $r_1 = r_2 = 1$), excessive alternating behavior occurs. If the value of reactivity ratio of one monomer thoroughly exceeds the other (i.e. $r_1 \gg r_2$), the consecutive homopolymerization of one monomer is followed by homopolymerization of the second that consists of a blocky type copolymer.[32] In this work, copolymer compositional plots were obtained from the spectroelectrochemical experimental data. The correlation between the copolymer composition, *F* and the feed monomer molar ratio, *f*, is given in Table 1. In order to determine the reactivity ratio of SNS-Fc and EDOT, Fineman–Ross copolymerization equations was used.[33] In the Fineman–Ross method, the equation $f_i/F_i\,(1 - F_i) = r_2 - r_1\,(f_i^2/F_i)$ is used. The Fineman–Ross plot for the copolymerization of SNS-Fc with EDOT performed at 1.5 V constant potential is depicted in Figure 5. A plot of $f_1(1 - F_1)/F_1$ as ordinate and f_i^2/F_1 as absciss a is a straight line whose slope is $r_{\text{SNS-Fc}}$ and whose intercept is r_{EDOT}. The monomer reactivity ratios were calculated to be; r_1 (SNS-Fc) = 1.03 and r_2 (EDOT) = 0.61.

This result indicates that SNS-Fc shows higher activity as compared to EDOT and (SNS-Fc) enter copolymer structure



Scheme 1. Synthesis and polymerization of SNS-Fc.

more than (EDOT). Furthermore, copolymer composition F_1 and monomer feed ratio f_1 using drawn graphics are shown in Figure 6. In Figure 6, F_1 larger than f_1 and the curve is above the diagonal. It is consistent with the value of r_1 and r_2 ($r_{1>1}$ and $r_{2<1}$).

3.4. Effect of applied potential for copolymerization polymerization

To investigate effects of the applied potential on copolymerization, copolymers were synthesized with different polymerization potentials, but, the same co-monomer feed ratio. A specific monomer feed ratio was selected to investigate the effect of applied potential for copolymerization. For this purpose, P(SNS-Fc-*co*-EDOT) copolymer D (1/4 feed ratio) was chosen to be effective in copolymerizing. Different applied potentials (1.0, 1.3, and 1.5) were applied solution of D to investigate the effect applied potential on copolymerization. Spectroelectrochemical and optical properties of copolymers were investigated in monomer free system. Spectroelectrochemistry studies were carried out in turn to show the differences in (λ_{max}) for the samples. Figure 7 represents the spectra of copolymers in neutral state where a gradual shift and a broadening of peak were observed with increasing polymerization potential. When the polymerization potential is increased, the band gap energy decreases. In addition to spectroelectrochemistry studies, results indicated that there is a direct relation between the color of the polymer in the neutral state and increasing the potential applied in the copolymer. As the applied potential increases, the resulting copolymer multi-electrochromic feature arises. Table 2 shows copolymers prepared different applied potential and theirs optical properties. According to spectroelectrochemical results, as the potential of the polymerization rise, the amount of PEDOT of the copolymer composition rises. As a result, the important changes in the optical properties of copolymers were obtained.

3.5. Switching

Rapid and consistent color change of material is crucial for electrochromic application. For investigation of optic contrast and switching time, square-wave potential step method coupled with optical spectroscopy is used. In this study, polymer switched constantly between two different potentials with a set period of time (5s).

The polymer film was synthesized on ITO-coated glass slides. During the experiment, for P(SNS-Fc-*co*-EDOT) copolymer maximum contrast was obtained in 560 and 1000 nm. Optic contrast (ΔT) of P(SNS-Fc-*co*-EDOT) was found 47% at 560 nm and 33% at 1000 nm in Figure 4(d). Switching time of P(SNS-Fc-*co*-EDOT) was found as 1.98 s at 560 nm and 2.22 at 1000 nm, respectively (Figure 8).

4. Conclusion

In this study, ferrocene-functionalized conducting metallopolymer was synthesized and its spectroelectrochemical properties were investigated. Copolymerization of SNS-Fc and EDOT has been studied by electrochemical methods. Due to the combined properties of monomers, there is an improvement in the electrochemical properties of the copolymer with the incorporation of EDOT. Electropolymerization is controlled by applying potential values and monomer feed ratio. As applied copolymerization potentials were increased, maximum wavelengths of obtaining copolymers were red shifted. This is due to increasing EDOT in the copolymer composition as applied potential increase and band gap (E_g) of the copolymer decreases. Electrochromic properties of homopolymers and copolymers were comparatively investigated. We also approximately calculated copolymer composition and the monomer reactivity ratios by using the spectral data. It was found that feed ratio of the SNS-Fc was decreasing, reactivity ratios is close to unity so it can be said to be ideal copolymerization. In higher feed ratio of SNS-Fc, reactivity ratio is greater than unity. This indicates that copolymer contains more SNS-Fc than EDOT.

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References

[1] Taouil AE, Husson J, Guyard L. Synthesis and characterization of electrochromic [Ru(terpy)2 selenophene]-based polymer film. J. Electroanal. Chem. 2014;728:81–85.
[2] Encinas S, Flamigni L, Barigelletti F, et al. Electronic energy transfer and collection in luminescent molecular rods containing ruthenium(II) and osmium(II) 2,2′:6′,2′-terpyridine complexes linked by thiophene-2,5-diyl spacers. Chem. – Eur. J. 2002;8:137–150.
[3] Soganci T, Ak M, Ocal S, et al. Ferrocenyldithiophosphonate containing conducting polymers and theirs electrochromic application. J. Inorg. Organomet. Polym. Mater. 2015;25:1011–1018.
[4] Ayranci R, Ak M, Ocal S, et al. Synthesis of new ferrocenyldithiophosphonate derivatives: electrochemical, electrochromic, and optical properties. Des. Monomers Polym. 2016;5551:1–8.

[5] Karakus M, Ikiz Y, Kaya HI, et al. Synthesis, characterization, electrospinning and antibacterial studies on triphenylphosphine-dithiphosphonates Copper(I) and Silver(I) complexes. Chem. Cent. J. 2014;8:18.

[6] Kwak YH, Lee J, Lee J, et al. A simple and low-cost biofilm quantification method using LED and CMOS image sensor. J. Microbiol. Methods. 2014;107:150–156.

[7] Skabara PJ. A brief perspective on the evolution of plastic electronics – from highly conducting polymers to conjugated organic semiconductors. Chem. Commun. 2013;49:9242–9244.

[8] Ak M, Yigitsoy B, Yagci Y, et al. Gas sensing property of a conducting copolymer. E-Polymers. 2007;7:495–502.

[9] Lelii C, Bawendi MG, Biagini P, et al. Enhanced photovoltaic performance with co-sensitization of quantum dots and an organic dye in dye-sensitized solar cells. J. Mater. Chem. A. 2014;2:18375–18382.

[10] Österholm AM, Shen DE, Kerszulis J, et al. Tuning of electrochromic polymer blends toward high-contrast eyewear. ACS Appl. Mater. Interfaces. 2015;7:1413–1421.

[11] An C, Li M, Marszalek T, et al. Thiadizoloquinoxaline-based low-bandgap conjugated polymers as ambipolar semiconductors for organic field effect transistors. Chem. Mater. 2014;26:5923–5929.

[12] Memioglu F, Öznülüer T, Ak M. Conducting carbon/polymer composites as a catalyst support for proton exchange membrane fuel cells. Int. J. Energy Res. 2014;38:1278–1287.

[13] Kart SÖ, Tanboğa Ebru, Soyleyici HC, et al. Theoretical study of the structure-properties relationship in new class of 2,5-di(2-thienyl)pyrrole compounds. Spectrochim. Acta. A. Mol. Biomol. Spectrosc. 2014;137C:1174–1183.

[14] Ayranci R, Demirkol DO, Ak M, et al. Ferrocene-functionalized 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl) aniline: a novel design in conducting polymer-based electrochemical biosensors. Sensors. 2015;15:1389–1403.

[15] Oyman G, Geyik C, Ayranci R, et al. Peptide modified conducting polymer as biofunctional surface: monitoring of cell adhesion and proliferation. RSC Adv. 2014;4:53411–53418.

[16] Soganci T, Demirkol DO, Ak M, et al. A novel organic–inorganic hybrid conducting copolymer for mediated biosensor applications. RSC Adv. 2015;4:46357–46362.

[17] Kazemi SH, Mohamadi R. Electrochemical fabrication of a novel conducting metallopolymer nanoparticles and its electrocatalytic application. Electrochim. Acta. 2013;109:823–827.

[18] Ak M, Cetişli H, Toppare L. Blend or copolymer? Spectroelectrochemical evidence of copolymerization and blending of two electrochromic monomers. Colloid Polym. Sci. 2012;291:767–772.

[19] Kerszulis J, Johnson KE, Kuepfert M, et al. Tuning the painter's palette: subtle steric effects on spectra and colour in conjugated electrochromic polymers. J. Mater. Chem. C. R. Soc. Chem. 2015;3:3211–3218.

[20] Yang H, Zhang L, Fu Z, et al. Comonomer effects in copolymerization of ethylene and 1-hexene with MgCl2-supported Ziegler-Natta catalysts: new evidences from active center concentration and molecular weight distribution. J. Appl. Polym. Sci. 2014;132:41264(1–8).

[21] Sydorov D, Duboriz I, Pud A. Poly(3-methylthiophene)-polyaniline couple spectroelectrochemistry revisited for the complementary red-green-blue electrochromic device. Electrochim. Acta. 2013;106:114–120.

[22] Ak M, Tanyeli C, Akhmedov IM, et al. Optoelectrochemical properties of the copolymer of 2,5-di(4-methylthiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole monomer with 3,4-ethylenedioxythiophene. Thin Solid Films. 2008;516:4334–4341.

[23] Ak M, Şahmetlioğlu E, Toppare L. Synthesis, characterization and optoelectrochemical properties of poly(1,6-bis(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexane) and its copolymer with EDOT. J. Electroanal. Chem. 2008;621:55–61.

[24] Groenendaal L, Jonas F, Freitag D, et al. Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future. Adv. Mater. 2000;12:481–494.

[25] Yildirim A, Tarkuc S, Ak M, et al. Synthesis of electroactive layers based on functionalized anthracene for electrochromic applications. Electrochim. Acta. 2008;53:4875–4882.

[26] Jagan Mohan D. Synthesis, characterization and swelling properties of copolymers of N(-1,1-dimethyll-3-oxobutyl) acrylamide with methyl methacrylate. Des. Monomers Polym. 2014;17:438–444.

[27] Yang YL, Lee YH, Lee YP, et al. Synthesis and characterization of poly(3-hexylthiophene)-poly(3-hexyloxythiophene) random copolymers with tunable band gap via Grignard metathesis polymerization. Polym. Int. 2014;63:2068–2075.

[28] Miozzo L, Battaglini N, Braga D, et al. Synthesis and characterization of all-conjugated copolymers of 3-hexyl-thiophene and EDOT by grignard metathesis polymerization. J. Polym. Sci. Part A: Polym. Chem. 2012;50:534–541.

[29] Lejars M, Margaillan A, Bressy C. Synthesis and characterization of diblock and statistical copolymers based on hydrolyzable siloxy silylester methacrylate monomers. Polym. Chem. 2014;5:2109–2117.

[30] Erbil C, Terlan B, Akdemir Ö, et al. Monomer reactivity ratios of N-isopropylacrylamide-itaconic acid copolymers at low and high conversions. Eur. Polym. J. 2009;45:1728–1737.

[31] Tsubokawa N, Abe N, Wei G, et al. Grafting of polymers onto a carbon-fiber surface by ligand-exchange reaction of poly(vinyl ferrocene-co-vinyl monomer) with polycondensed aromatic rings of the surface. J. Polym. Sci. Part A: Polym. Chem. 2002;40:1868–1875.

[32] Lartey M, Gillissen M, Adzima BJ, et al. Synthesis and reactivity ratios of regioisomeric vinyl-1,2,3-triazoles with styrene. J. Polym. Sci. Part A: Polym. Chem. 2013;51:3359–3364.

[33] Borisova O, Billon L, Zaremski M, et al. Synthesis and pH- and salinity-controlled self-assembly of novel amphiphilic block-gradient copolymers of styrene and acrylic acid. Soft Matter. 2012;8:7649–7659.