



# An investigation on electrochromic properties of new copolymers based on dithienylpyrrole and propylenedioxythiophene



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## ABSTRACT

In this research, the effect of ProDOT (3,4-propylenedioxythiophene) monomer on the electrochromic properties of dithienylpyrrole type copolymer has been studied. The copolymers of these two components have obtained by electroanalytical methods in different monomer ratios. The morphological, optical and electrochemical characterizations of all copolymers were investigated. The electrochromic properties of the novel films were investigated by cyclic voltammetry and spectroelectrochemical methods. Different colors of the electrochromic films were achieved under different applied potentials. The maximum difference of the UV–vis absorption of the film was found about 42% between  $-0.6$  V and  $1.2$  V at  $850$  nm for P(C3) copolymer with a fast switching time ( $0.4$  s). The morphological and chemical analyses for copolymers were also detected.

## 1. Introduction

Since the discovery of the idea about conducting polymers, they have been applied widely for electrical fields, such as sensors [1], supercapacitors [2], solar cells [3,4], and electrochromic devices [5–8] because of their environmental friendless, recyclable ability, easy fabrication and fast redox mechanism [9–12]. In addition to all of these properties, conducting polymers have also fast switching, high coloration efficiency and multicolor obtainability on different redox states during usage for electrochromic devices [13–15]. Considering to these redox states, there are fortunately some techniques, which have been used to improve the electrochromic properties of conducting polymers in the last years. One of these techniques is modification of polymer backbone with substitute groups. This modification improves the colorimetric properties of post modified electrochromic polymers because of these substitute groups affecting the conjugation length and electron density of polymer backbone [16]. Another technique is blending or copolymerization, which is an easy and facile method used in order to tune the electrochromic properties of the conjugated polymers [17].

The intrinsic conjugated polymers used in electrochromic devices are mostly polythiophene [7,17], polypyrrole [18], polyaniline [19],

polycarbazole [20] and polyfluorene [21] based aromatic based materials. A hybrid monomer, namely, dithienylpyrrole (SNS) based on thiophene and pyrrole was firstly synthesized and electropolymerized by Otero et al. [22–23]. A series of studies came in succession and new SNS derivatives with different substitute groups were synthesized and electrochemically polymerized. The results showed that this trimeric hybrid structure ensures lower oxidation potentials than its each components and its middle pyrrole unit gives functionalization chance of the resulted polymer and so enables processability and tunability of the polymer [22–33]. Many N-alkyl or aromatic substituted SNS derivative polymer films (P(SNS)) have been synthesized so far [28–33]. Our group was also synthesized and electropolymerized some different substituted N-functionalized SNS derivatives, such as phthalonitrile [31], phthalocyanine [32] and halo-aromatic substituted groups [33]. Furthermore, lots of studies have been done related copolymerization of SNS derivatives. This popularity of co-electropolymerization of SNS derivatives has begun with the different N-functionalized SNS trimeric structure with 3,4 ethylenedioxythiophene (EDOT) by many research groups [34–38]. Just like EDOT polymer, 3,4 propylenedioxythiophene (ProDOT) polymer is also almost transparent in the doped state, which enables a door during usage in electrochromic devices as a cathodically

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coloring material. Furthermore, ProDOT polymeric films (66%) show higher contrast ratio than PEDOT (54%) [39]. Until now, SNS and ProDOT based copolymer synthesis and its electrochromic and electrochemical properties have not been reported.

Hence, in this study we want to share our experiences of the copolymerization of SNS structure with ProDOT unit and effects of this donor unit on the electrochemical and optical properties in detail, for the first time. The morphological, chemical structure, electrochemical and optical studies were also investigated for new synthesized copolymers.

## 2. Experimental

### 2.1. Materials

All chemicals were used from Sigma Aldrich without further purification. 1-phenyl-2,5-di(thiophen-2-yl)-1H-pyrrole (SNS-PN), monomer was synthesized according to reference [27]. For the copolymerization process 10 mM ProDOT and 10 mM SNS-PN were used in different monomer ratios. Acetonitrile (ACN) as a solvent and 0.1 M lithium perchlorate ( $\text{LiClO}_4$ ) as a supporting electrolyte were used during electropolymerization and electrochemical and optical characterizations of copolymer films. A typical three electrode system was used for the all studies. For the polymerization of monomers, Platinum disc ( $0.02 \text{ cm}^2$ ), Platinum wire and Ag/AgCl were used as working electrode, counter electrode and reference electrode respectively. For spectroelectrochemical analysis, UV cuvette was used as holder and an indium-tin oxide (ITO, Delta, Tech. 8–12  $\Omega$ ,  $0.7 \text{ cm} \times 5 \text{ cm}$ ), Ag and Pt wires were used as working electrode, reference electrode and counter electrode, respectively.

### 2.2. Equipments

Ivium compactstat potentiostat device was used for the electrochemical studies. An Ivium Stat electrochemical analyzer was used for electrochemical and in situ optical studies. Spectroelectrochemical studies were carried out with a Specord S600 spectrometer and colour space was given by the International Commission of Illumination with luminance (L), hue (a), and intensity (b). FTIR spectra were recorded on Bruker Equinox 55 with an attenuated total reflectance (ATR). An AFM (Atomic force microscopy) from Nanomagnetics Instruments was used for investigating the morphologies of the films under ambient conditions.

## 3. Result and discussion

### 3.1. Electrochemical copolymerization and characterization

It is important to determine a suitable oxidation potential for the electrocopolymerization process of different two monomers. Before the revelation of oxidation potential range of monomer and comonomer mixtures, we mixed the SNS-PN and ProDOT monomer concentration (each has a total concentration of 10 mM) as 10:1 (C1), 2:1 (C2) and 1:1 (C3) in order to grow copolymer on FTO as using multiple CV curves in 0.1 M  $\text{LiClO}_4$  and ACN medium on Pt disc electrode at a scan rate of  $100 \text{ mV s}^{-1}$  (Fig. 1). As seen in Fig. 1, while the first oxidation potentials at about 0.75 V for comonomers mixture belongs to the SNS-PN unit, another second oxidative onset peaks in the potential range between 1.1 V to 1.2 V has been observed due to the oxidation of

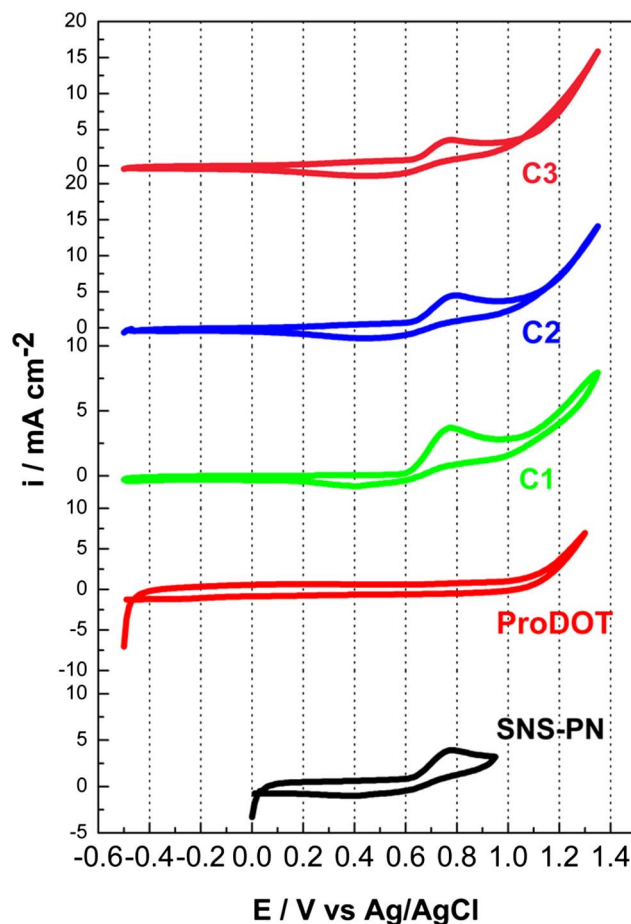


Fig. 1. The oxidation potential comparisons of the SNS-PN, ProDOT, C1, C2 and C3 monomers in the medium of 0.1 M  $\text{LiClO}_4$  in ACN with a scan rate of  $200 \text{ mV s}^{-1}$ .

ProDOT unit in the comonomer mixture solution.

All measurements were determined to be a total of 15 cycles with CV method in order to synthesize homopolymers (SNS-PN in Fig. 2(a); ProDOT in Fig. 2(i)) and copolymers (C1 in Fig. 2(c), C2 in Fig. 2(e), C3 in Fig. 2(c)) successfully. Then, the film behaviors of all polymers coated onto the Pt disc electrode (P(SNS-PN) in Fig. 2(b); P(C1) in Fig. 2(d), P(C2) in Fig. 2(f), P(C3) in Fig. 2(g) and P(ProDOT) in Fig. 2(h)) were investigated at  $200 \text{ mV s}^{-1}$  in monomer free medium. As shown in Fig. 2, both copolymer formations and film behaviors were different than homopolymer synthesis and formations CV diagram. Furthermore, as the amount of ProDOT concentration in the structure, the oxidation potentials of copolymer P(C3) shifts to right and shows capacitive behaviour than other copolymers (P(C1) and P(C2)). As the monomer ratio concentration changed on copolymerization process, different redox characters were seemed on CV measurements.

In order to analyze kinetic behaviour of coated copolymer films on the surface of bare Pt disc electrode, the electrochemical behaviors of the copolymer films in different scan rates between  $20 \text{ mV s}^{-1}$  and  $200 \text{ mV s}^{-1}$  in monomer free medium were investigated. As the scan rate increases for all copolymers, anodic and cathodic peak current densities ascends, indicating non-diffusional kinetic behaviour for copolymers (Fig. 3).

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