



An Amide Substituted Dithienylpyrrole Based Copolymer: Its Electrochromic Properties

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Electrochemistry of a new generation copolymer of N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-4-(vinyloxy) benzamide (TPVB) and 3,4-ethylenedioxythiophene (EDOT) is presented. In this study, a novel copolymer based upon TPVB and EDOT is successfully synthesized and characterized in dichloromethane (DCM)/tetrabutylammonium hexafluorophosphate (TBP₆) solution for different feed ratios of monomers via electrochemical methods. The copolymer film reveals three different colors (pale red color, green, midnight blue) under different potentials and it has good optical contrasts (44% at 555 nm and 75% at 1000 nm) and fast switching times (1.5 s at 555 nm and 2.0 s at 1000 nm). Satisfactory results implied that the copolymer films (P(TPVB-co-EDOT)) can be used in a wide variety of applications such as electrochromic devices, optical displays. We also describe a proposal for the determination of copolymer composition by means of the optical properties of P(TPVB-co-EDOT).

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Significant research efforts in the last years have been dedicated to the design and synthesis of novel functional polymers for optoelectronic and sensor applications.^{1,2} Dithienylpyrrole (SNS) is one of the most widely used functional monomer for this purpose.^{3–11} For example, ferrocene functionalized poly(dithienylpyrrole) P(SNS) was used for the detection of glucose which is a biologically important redox-active molecule.¹² In addition, amine group functionalized SNS derivative can be used as a coating material for cell culture applications.¹³

Three primary strategies have been used for altering the electrochromic properties of the conducting polymers: (1) design of the monomers previous to polymerization (2) carrying out the copolymerization with different monomers, and (3) arrangement of hybrid materials.¹⁴ Among them, copolymerization is a significant method to achieve much better features. Poly(3,4-ethylenedioxythiophene) (PEDOT) is frequently encountered in copolymers due to its rapid switching and good stability in its doped form.¹⁵ Recently, in order to improve the properties of the PEDOT, many workers focused on its copolymers with different monomers.^{5,16–25}

Composition of copolymer is an important parameter in determining their properties which is crucial for practical applications. Determining the concentrations of the monomers and their reactivities are of several ways to predict copolymer composition. The estimation of copolymer composition and determination of monomer reactivity ratios are especially difficult for the insoluble conducting copolymers.^{10,26,27}

In this work, a new monomer, N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-4-(vinyloxy) benzamide (TPVB) was synthesized and characterized. Copolymers based on TPVB and EDOT have been successfully synthesized via electrochemical methods with different monomer feed ratios. We also describe a proposal to determine copolymer composition by means of the optical properties of P(TPVB-co-EDOT).

Experimental

Equipments.— The FTIR spectra were recorded on a Perkin Elmer FT-IR spectrometer. Ivium Compactstat potentiostat/galvanostat was used for electrochemical synthesis and cyclic voltammetry experiments. An Agilent 8453 UV-vis spectrophotometer was used to conduct the spectroelectrochemical studies of the conducting polymers.

Synthesis of monomer.— The reagents; 1,4-di(2-thienyl)-1,4-butanedione and 4-(vinyloxy)benzohydrazide were prepared in accordance with the methods in the literature.^{10,28} All experiments were executed under dry argon using Standard Schlenk techniques. Solvents were dried, distilled and saturated with argon. The monomer

(TPVB) was synthesized from 1,4-di(2-thienyl)-1,4-butanedione and 4-(vinyloxy)benzohydrazide in the presence of catalytically amount of p-toluenesulfonic acid (PTSA). A round bottomed flask equipped with an argon inlet and magnetic stirrer was charged with 1 g (4 mmol) 1,4-di(2-thienyl)-1,4-butanedione, 0.72 g (4 mmol) 4-(vinyloxy)benzohydrazide, 35 mg (0.2 mmol) PTSA, 0.2 mL DMSO and 50 mL toluene. The resultant mixture was stirred and refluxed for 24 h under argon. Hot dark solution was filtered to remove oily products. Then, the mixture was cooled to room temperature and the solid product was filtered to give a green powder. The product was washed with pentane (3 × 15 mL) and air dried to yield 1.5 g 96% (mp 187–191°C). The synthetic route of the monomer is shown in Scheme 1. The structure of the monomer was confirmed by ¹H NMR and ¹³C NMR spectral analyses. ¹H NMR and ¹³C NMR spectra of TPVB were recorded with dimethyl sulfoxide (DMSO) as the solvent in room temperature with a Bruker-Instruments-NMR Spectrometer (DPX-400), operating at 400 MHz. The ¹H-NMR and ¹³C-NMR spectra of the monomer have the characteristic peaks of the structure.

¹H-NMR (400 MHz, 25°C, in DMSO-d₆) 11.82 δ (s; 1H^e, -NH-), 7.96δ (d; 2H^d), 7.37δ (d; 2H^f), 7.26δ (d; 2H^b), 7.12δ (t; 2H^g), 7.01δ (d; 2H^c), 6.57δ (s; 2H^h), 6.05δ (br s; 1H^b), 5.35δ (2H^a).

¹³C-NMR (101 MHz, DMSO) δ 165.91 (s), 161.98 (s), 133.68 (s), 132.82 (d, *J* = 3.0 Hz), 130.17 (s), 129.37 (s), 127.76 (s), 124.94 (s), 123.71 (d, *J* = 3.1 Hz), 118.38 (s), 115.21 (s), 107.25 (s), 68.89 (s).

Elemental analysis: C, 64.19; H, 4.13; N, 7.62; S, 16.24.

Electrochemical synthesis of P(TPVB-co-EDOT).— All of the electrochemical experiments were performed using a TBP₆/DCM supporting electrolyte-solvent couple at room temperature. 10⁻² M of TPVB was dissolved in 0.1 M TBP₆ in DCM and 10⁻² M of EDOT were introduced into a single compartment electrolysis cell for the synthesis of conducting copolymer (Scheme 1). The copolymer was potentiostatically (at 1.5 V) deposited on ITO.

Results and Discussion

Structural characterization.—**FTIR analysis of TPVB-co-EDOT.**— FTIR spectrum of electrochemically synthesized P(TPVB-co-EDOT) have characteristic peaks: 3164 cm⁻¹ (N–H stretching), 3082 cm⁻¹ (CH₂=CH- stretching), 1674 cm⁻¹ (C=O stretching). Characteristic peaks of the monomer remained unperturbed upon electrochemical polymerization. The intensity absorption bands of the monomer at 2991 cm⁻¹ arising from C–H α stretching of thiophene moiety, disappeared completely. This is an evidence of the polymerization from 2,5 positions of thiophene moiety of the monomer. Besides, formation of a new peak was observed at 1397 cm⁻¹ due to the presence of aromatic ethylenedioxy group. According to the FTIR studies, copolymer of the TPVB with EDOT was successfully synthesized.

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