BOOK OF ABSTRACTS

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Blend or copolymer? Spectroelectrochemical evidence of copolymerization or blending two monomer

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Conducting polymers have attracted great interest due to their ease of synthetic accessibility and modified architecture which can control the polymer properties (i.e., electronic, optical, conductivity, etc.) [1]. These advanced systems can be modified to be amenable for use in the desired application by changing the structure of starting monomers. Blending and copolymerization are another frequently used methods in order to improve the properties of the polymers [2].

A dipyrromethane functionalized monomer; 5-(4-*tert*-butylphenyl) dipyrromethane (BPDP) was synthesized. Electrochemical polymerization, copolymerization and blending of BPDP with 3,4-ethylenedioxythiophene (EDOT) were achieved in $LiClO_4$/AN. Spectral and electrochromic properties of producs are investigated. Spectral properties of copolymer and blend have great differences from each other and corresponding homopolymers. Effects of differentiation feed ratio of monomers on copolymers' spectral properties are also investigated.

1- Terje A. Skotheim ,Handbook of Conducting Polymers, II. Ed. Marcel Dekker, 1998.
2- O. Turkaslan, M. Ak, C. Tanyeli, I. M. Akhmedov and L. Toppare, "J. Polym. Sci., Part:A Polym. Chem., 45(19), 2007, 4496-4503.

BLEND OR COPOLYMER? SPECTROELECTROCHEMICAL EVIDENCE OF COPOLYMERIZATION OR BLENDING TWO MONOMER

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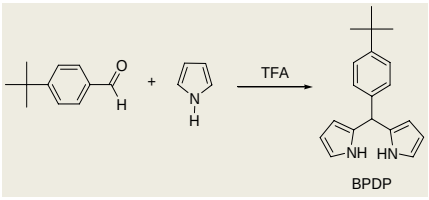
Introduction

Conducting polymers have attracted great interest due to their ease of synthetic accessibility and modified architecture which can control the polymer properties (i.e., electronic, optical, conductivity, etc.) [1]. These advanced systems can be modified to be amenable for use in the desired application by changing the structure of starting monomers. Blending and copolymerization are another frequently used methods in order to improve the properties of the polymers [2].

Synthesis of BPDP

Synthesis of 5-(4-*tert*-butylphenyl)dipyrromethane (BPDP) [3].

5-(4-*tert*-butylphenyl)dipyrromethane was synthesized according to literature [3-4] (Scheme 1) (1.66 g, 33 %, mp 160-163 °C) BPDP was characterized with NMR spectroscopy (Fig 1-2).



Scheme1: Synthesis route of BPDP

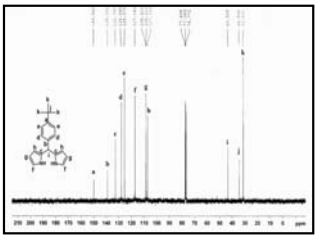


Figure 1:C13-NMR spectrum of BPDP

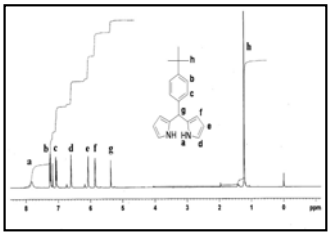


Figure 2: 1H-NMR spectrum of BPDP

Cyclic Voltammetry

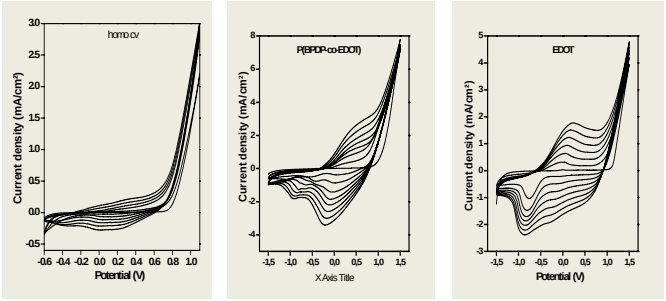
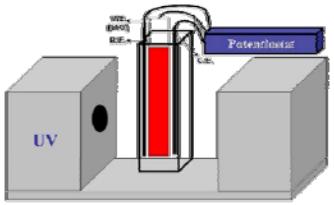


Figure 3: Cyclic Voltammetry Graphs of P(BPDP), P(BPDP-co-EDOT) and PEDOT

The oxidation/reduction behaviors of monomer and polymer were investigated by cyclic voltammetry (CV) using 0.1 M LiClO4/AN supporting electrolyte/solvent couple. Experiments were carried out in an electrolysis cell equipped with ITO coated glass plate as the working, Pt wire counter and Ag wire pseudo reference electrodes. Figure 3 shows cyclic voltammetry graphs of P(BPDP), P(BPDP-co-EDOT) and PEDOT.

Spectroelectrochemistry

The best way of examining the changes in optical properties of conducting polymers upon voltage change is via spectroelectrochemistry (Fig 4). It also gives information about the electronic structure of the polymer such as band gap (Eg) and the intergap states that appear upon doping. The onset energy for the π-π^* transition (electronic band gap) was 2.39 eV and λmax was found to be 364 nm from spectroelectrochemistry of P(BPDP) film (Fig 5).



Figue 4: Experimental setup of the spectroelectrochemical investigations

Feed Ratio Investigation

The band gap energies and absorption maxima of the copolymers are different than the values for PEDOT and P(BPMP) as expected. In addition, the λ_{max} values of the copolymers are red shifted when compared with 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 and Py units. (Fig 6)

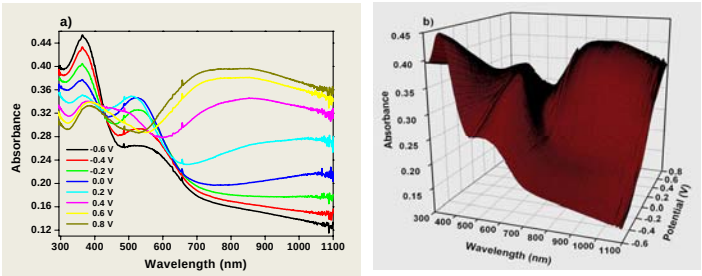


Figure 5 : Spectroelectrochemistry of P(BPDP) film a) (2D) b) (3D)

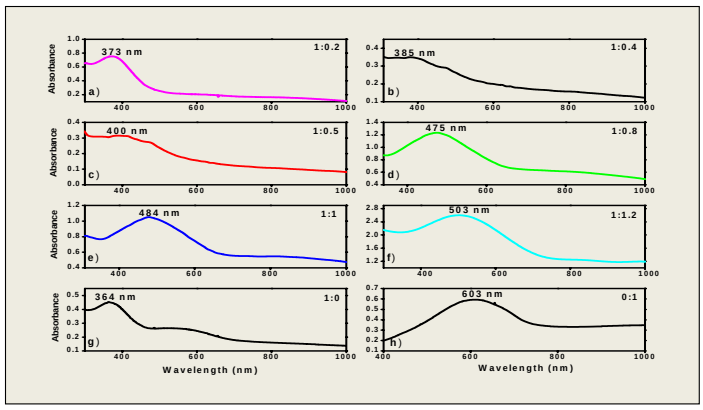


Figure 6: Spectroelectrochemistry of P(BPDP-co-EDOT) film prepared different feed ratio of monomers

For investigation of difference between spectral properties of copolymer and compozite, P(EDOT)-P(BPDP) compozite was prepared. For this purpose firstly EDOT polymerized on ITO coated glass electrode and than BPDP polymerized on this electrode. Spectroelectrochemistry of compozite is shown in Fig.7a and UV spectrum of copolymer and compozite (Neutral states) is shown in Fig.7b for comparison. Copolymer has only one λ_{max} value but compozite has two different λ_{max} values.

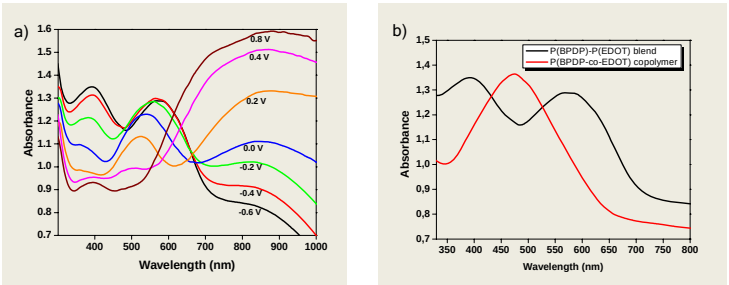


Figure 7: a)Spectroelectrochemistry of compozite film b)UV Spectra of copolymer film

Conclusions

- ❑ BPDP was synthesized and characterized.
- ❑P(BPDP), P(EDOT), P(BPDP-co-EDOT) and P(BPDP)-P(EDOT) polymer films synthesized and characterized succesfully..
- ❑ Redox properties of these polymers were investigated by CV.
- ❑ Polymer films synthesized on ITO electrode and spectroelectrochemical properties were investigated. π-π^* transition wavelength of P(BPDP) fim was found to 354 nm and band gap was found to 2.39 eV.
- ❑ Spectroelectrochemical properties of copolymers prepared by using different feed ratio of monomers were investigated.
- ❑ It is found that, whereas copolymer has only one λ_{max} value, compozite has two different λ_{max}.

References

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