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Synthesis and Spectroelectrochemical Characterization of an Electrochromic Phosphole-EDOT Copolymer: poly([1-phenyl-2,5-bis(2-thienyl)thioxophosphole]$_{0.14}$ -co- [3,4-ethylendioxythiophene] $_{0.86}$)

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Summary

We report the synthesis of an electrochromic phosphole-ethylendioxythiophene (EDOT) copolymer, poly(1-phenyl-2,5-bis(2-thienyl) thioxophosphole (**1**) -co- 3,4-ethylendioxythiophene (**2**)). This phosphole-EDOT copolymer, (**3**), with a content of (**1**) of 14 mol % showed an oxidation potential of 0.6 V, significantly lower than that of poly(**1**) (1.3 V) but higher than that of poly(**2**) (0.16 V). The copolymer (**3**) exhibited an UV/Vis/NIR absorption maximum at 715 nm which is red shifted compared to poly(**1**) (Δλmax = 200 nm) and blue shifted compared to poly(**2**) (Δλmax = 135 nm). Copolymer (**3**) presents a narrower optical band gap than poly (**1**) as a consequence of association in the copolymer of electron-rich heterocycles (**2**) with low-lying LUMO repeat units (**1**) resulting in intramolecular charge transfer and delocalization of the π-system. FTIR and XPS spectroscopic data for the phosphole-EDOT copolymer (**3**) are consistent with the expected copolymer structure and TGA data showed an increased stability of the material compared to that of neat poly(**2**). Copolymer (**3**) displays blue-to-black electrochromic behavior, with a maximum optical contrast of 13 % in the visible region and 15 % in the NIR region. Spectroelectrochemical measurements demonstrate a band at 429 nm (dedoped structure) and the emergence of a new one at 575 nm (doped structure) upon oxidation. Finally, morphological characterization of copolymer (**3**) by AFM depicts aggregated spherical particles of 100 – 250 nm in size with a RMS roughness of 123 nm, smaller than that observed for poly(**2**) under the same synthetic conditions.

Keywords

phosphole, edot, copolymer, electrochromic

Introduction

Electrochromism is a property that is found in a great number of materials which exhibit different electronic absorption spectra depending on their redox states. During the redox process, new bands are generated in the visible region leading to a color change in the material. This property was first reported by Deb in 1969 [1] in an inorganic oxide (WO_3). Since this discovery, other electrochromic materials such as mixed-valence metal complexes, organic small molecules and intrinsically conducting polymers, have been studied intensively [2, 3].

The conducting polymers are an interesting class of electrochromic materials because they offer the advantages of being synthesized on flexible substrates as compared to conventional electrically conductive inorganic materials [4], wide range of colors, fast switching time [5] and more simple, inexpensive techniques for the preparation of films. In addition, small structural changes in the monomer provide a tunable oxidation state and band gap in the polymer allowing the possibility of color design [6]. In this field, the most investigated polymers have been polypyrrole, polyaniline, polythiophene and poly(3,4-ethylenedioxythiophene) (PEDOT) [7] as well as their derivatives.

PEDOT has become one of the most attractive conductive polymers because of its high electrical conductivity, transparency and structural stability [8, 9]. As a consequence of its excellent properties, PEDOT is being used in a great number of traditional and emerging applications including antistatic coatings, light-emitting diodes, capacitors, electrochromic, photovoltaic and sensor devices [8, 10]. In order to diversify the properties and expand the functions of these classical π-conjugated polymers, the incorporation of heteroatoms into the conjugated chain is expected to produce interesting properties. Examples of the incorporation of Lewis-basic σ^3,λ^3-phosphorus moieties in conjugated polymers are rare [11-15] even though the versatile reactivity of the P centers (nucleophilicity, coordination ability,…) [16-21] should allow a variety of postfunctionalizations. This point has been recently demonstrated with mixed phosphole-thiophene electroactive polymers [22]. Moreover several functionalized mixed phosphole-thiophene electroactive polymers can be easily synthesized by an electropolymerization process [11, 22-25].

Another way to diversify the properties of the classical π-conjugated polymers is to develop copolymers of conducting polymers leading to new materials with modulated properties. For instance, copolymerization of EDOT with EDOT derivatives or other monomers leading to new systems [26-28] with lower oxidation potential or smaller band gap has been described. In fact, copolymerization of EDOT with thiophene derivatives [29-31] allows modulation of electrochemical and optical properties of the resulting materials. In fact, copolymers of EDOT with simple heterocyclic monomers such as pyrrole (Py) [32,33] are good candidates for bio-applications. Interestingly, EDOT copolymers with N-methylpyrrole [34-36] depict a smaller band gap than the corresponding homopolymers making the material valuable for electro-optic applications.

In this article, we report the synthesis and characterization of an electrochromic phosphole-EDOT copolymer: poly([1-phenyl-2,5-bis(2-thienyl)thioxophosphole]$_{0.14}$-co-[3,4-ethylendioxythiophene]$_{0.86}$). This new electrochromic copolymer has been characterized by Cyclic Voltammetry (CV), Ultraviolet/Visible/Near-IR (UV-Vis-NIR) spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS), X-ray Photoelectron (XPS) spectroscopy, Thermogravimetric Analysis (TGA), Spectroelectrochemistry measurements and Atomic Force Microscopy (AFM).

Experimental

Materials

1-phenyl-2,5-di(2-thienyl)thioxophosphole (**1**) was synthesized following previously reported procedures [11, 23]. 3,4-Ethylenedioxythiophene (**2**) (Sigma-Aldrich), tetrabutyl-ammonium hexafluorophosphate (Fluka) and $LiClO_4$ (Sigma-Aldrich) were used as received. Dichloromethane (CH_2Cl_2) and acetonitrile (Sigma-Aldrich) were dried over P_2O_5 and distilled prior to use. Indium-tin oxide (ITO) plastic substrate was obtained from Sheldahl, with a resistivity of 20 Ω/sq.

Synthesis of poly([1-phenyl-2,5-bis(2-thienyl)thioxophosphole]$_{0.14}$-co-[3,4-ethylendioxythiophene]$_{0.86}$), copolymer (3)

The electrochemical copolymerization affording copolymer (**3**) was performed in a typical three electrode setup using an EC-Lab MPG Bio-logic multi-potentiostat employing both Pt sheet and ITO plastic as working electrodes, Pt sheet as counter electrode and Ag/AgCl as reference electrode. Electrochemical copolymerization was carried out by CV. The reaction mixture was a dry CH_2Cl_2 solution containing EDOT and (**1**) (80:20 molar ratio) with a total concentration of 0.05 M, and Bu_4NPF_6 (0.2 M) as supporting electrolyte. All experiments were carried out under an argon atmosphere.

Electrochemical and spectroelectrochemical characterization of copolymer (3)

Electrochemical characterizations of copolymer (**3**) on Pt and ITO sheets were carried out on a EC-Lab MPG Bio-logic multi-potentiostat, using monomer free 0.2 M Bu_4NPF_6/ CH_2Cl_2 solution. A monomer free 0.1 M $LiClO_4$/acetonitrile solution was used for the electrochromic characterization of the copolymer. Ag/AgCl was used as reference electrode, and Pt sheet as counter electrode. Pt sheet and ITO plastic were used as working electrodes. The spectroelectrochemical characterization of copolymer (**3**) was performed in an optical transparent thin layer electrode OTTLE cell using 0.1M $LiClO_4$/ acetonitrile solution. The potential was controlled using an EC-Lab MPG Bio-logic multi-potentiostat and the UV/Visible/Near-IR measurements were carried out in a UV/VIS/NIR V-570 JASCO spectrophotometer

Characterization techniques

The electrical conductivity of copolymer (**3**) was measured by a standard four-probe technique at room temperature. FTIR spectroscopy measurements were performed in a NICOLET AVATAR 360 spectrometer. The spectra of the as-grown copolymer (**3**) and PEDOT on an ITO plastic substrate have been recorded by the attenuated total reflectance (ATR) method using a ZnSe crystal. 128 scans were recorded for these spectra in the range of 4000 to 650 cm^{-1} with a 2 cm^{-1} spectral resolution. SEM and EDS measurements were carried out with a JEOL JSM 5500-LV microscope with a EDS IncaEnergy 200 from Oxford Instruments. X-ray photoelectron spectroscopy spectra were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg Ka (h = 1253.6 eV) 300-W X-ray source. Before recording the spectra, the sample was maintained in the analysis chamber until a residual pressure of ca. 5 x 10-7 N•m^{-2} was reached. The spectra were collected at pass energy of 50 eV. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Gaussian (70%) and Lorentzian (30%) lines. All binding energies (B.E.) were referenced to the C1's line at 284.6 eV, which provided binding energy values with an accuracy of ± 0.2 eV. High-resolution TGA scans have been recorded on a Hi-RESTM TGA Q500 (TA Instruments) apparatus under a highly pure nitrogen atmosphere at 40 ºC/min from 50 to 800 ºC. Prior to the TGA measurements, all the samples were dried under vacuum to avoid the presence of humidity. AFM images of the films were obtained with a Molecular Imaging "PicoPlus" atomic force microscope operating in acoustic mode for the solution-side of thin films of the samples on ITO substrate.

Results and discussion

Examples of electrochemical polymerization of phosphole-based monomers are very rare in the literature [11, 22, 25]. Mixed phosphole-thiophene electroactive polymers have been obtained by electropolymerization of thienyl-capped monomers containing 1,1'-diphosphole [25], thioxophosphole [11, 23, 24] and gold(I)-phosphole cores [22]. In all cases, an increase in current due to the deposits of the electroactive polymers on the working electrode was observed upon recurrent cycling. In this work, we describe electrochemical copolymerization experiments involving 1-phenyl-2,5-bis(2-thienyl)thioxophosphole (**1**) and 3,4-ethylenedioxythiophene (EDOT) (**2**). EDOT is a commonly used building block for the synthesis of conducting polymers [26]. The synthesis of copolymer (**3**) by CV is schematically depicted in Figure 1.

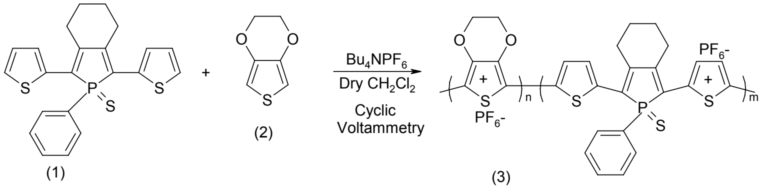

Figure 1. Illustration of the synthesis of phosphole-EDOT copolymer (**3**) (n=0.84, m=0.14) by Cyclic Voltammetry.

Electrochemical studies of monomer (**1**) and monomer (**2**) were carried out to determine their redox behavior using CV. The values of oxidation potential in a monomer free 0.1M $LiClO_4$/acetonitrile solution were similar for both derivatives [E_{ox}: 1.32 V for (**1**) and 1.6 V for (**2**) vs Ag/AgCl]. It is important to recall that the presence of the σ^4-phosphole ring of (**1**) does not perturb the classical chemistry of the thiophene rings [11, 23] since the tetracoordinated P-atom is inert. Hence, the terminal thienyl rings of (**1**) are oxidized in the classic way leading to the corresponding radical cation. The fact that monomers (**1**) and (**2**) are oxidized in the same potential range implies that the radical cations of both monomers are formed simultaneously at the working electrode surface. Hence, they can react together leading to copolymer (**3**) (Figure 1). This type of copolymerization is well documented in the literature [37]. For example, Reynolds' group has worked on the copolymerization of pyrrole with N-phenyl-pyrrole [39, 39] and in the copolymerization of carbazole-based polymers. [40, 41]. Similarly, 3,6-bis[2-(3,4-ethylenedioxythiophene)]-N-alkylcarbazole copolymers have been synthesized by electropolymerization of 2,2'-bis(3,4-ethylenedioxythiophene) and 3,6-bis-[2-(3,4-ethylenedioxy)thienyl]-N-methylcarbazole, where the two monomers exhibit similar oxidation potentials [27]. Also Santhosh et al carried out the polymerization of diphenylamine and m-toluidine [42] whereas a copolymer of 2,5-di(thiophen-2-yl)-1-p-tolyl-1H-pyrrole (DTTP) with 3,4-ethylene dioxythiophene (EDOT) has been reported by Yigitsoy [43].

Different combinations of electrolyte, monomer ratio and monomer concentration were investigated in order to obtain good quality films of poly(1-phenyl (2,5-bis(2-thienyl)thioxophosphole)-co-3,4-ethylenedioxythiophene) (copolymer (**3**)) by electropolymerization. The optimal conditions where found when copolymerization of monomers (**1**) and (**2**) was conducted in a dry CH_2Cl_2 solution containing Bu_4NPF_6 (0.2 M) as the supporting electrolyte and the two monomers in a molar ratio of (**2**)/(**1**) = 4/1 with a total concentration of 0.05 M. Upon successive scanning from -0.5 V to 1.8 V vs. Ag/AgCl at 25 mV/s, the formation of a blue electroactive polymeric film on the working electrode was observed. The obtained copolymer showed an electrical conductivity of $\sigma = 1.6\ (\pm 0.6) \times 10^{-4}$ S/cm.

The CV of copolymer (**3**) recorded in a monomer free CH_3CN solution shows an oxidation potential at 0.6 V vs. Ag/AgCl (Figure 2). This value is considerably lower than that recorded for poly(**1**) (ca. 1.3 V vs Ag/AgCl) [11, 23]. In addition, the CV of copolymer (**3**) also differs from that of poly(**2**) which shows an oxidation potential of 0.16 V vs. Ag/AgCl (Figure 1). This data supports the formation of copolymer (**3**) from monomer (**1**) and (**2**). It is interesting to note that the incorporation of the EDOT unit has a dramatic influence on the electrochemical properties. As already pointed out, copolymer (**3**) is much more easily oxidized than poly(**1**).

The relationship between the scan rate and peak current for copolymer (**3**) in a monomer free acetonitrile solution gave a linear fit (R > 0.99) (inset of Figure 2). This result shows that copolymer (**3**) is stable to p-doping whereas the reversibility of the oxidation process for poly(**1**) is only ca. 70% [23]. Note that this last result also shows that charge transport through the film is not diffusion limited or that there are no significant kinetic barriers to charging and discharging the film [44].

Theoretical calculations indicate that the IR absorption corresponding to the P-C=C vibration in phosphole compounds lies in the range between 700-640 cm^{-1} [45]. Figures 3A and 3C, corresponding to monomer (**1**) and copolymer (**3**), show clearly this IR absorption. Figure 3B, corresponding to PEDOT, exhibits the vibration bands characteristic of the EDOT ring. It shows bands at 1226 and 1028 cm^{-1}, which are associated with the C-O-C stretching vibration [46, 47]. In addition, vibrational bands are observed at 1528 and 1343 cm^{-1} originating from the stretching modes of C=C and C-C in the thiophene ring [48]. Copolymer (**3**) (Figure 3C) shows IR absorption bands from EDOT units and a strong and wide band at 1362 cm^{-1} which includes the C=C vibrations of EDOT and phosphole units. All these features suggest that copolymerization occurs during the CV electropolymerization of monomers (**1**) and (**2**).

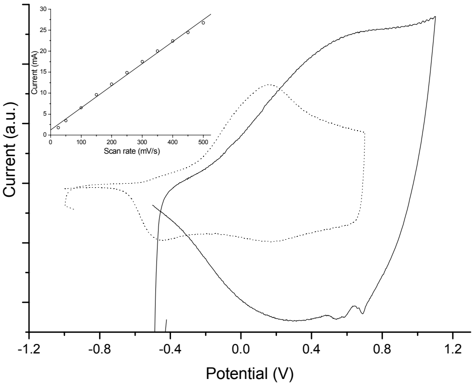

Figure 2. Cyclic voltagramms of PEDOT (········) and phosphole–EDOT copolymer (3)(——).

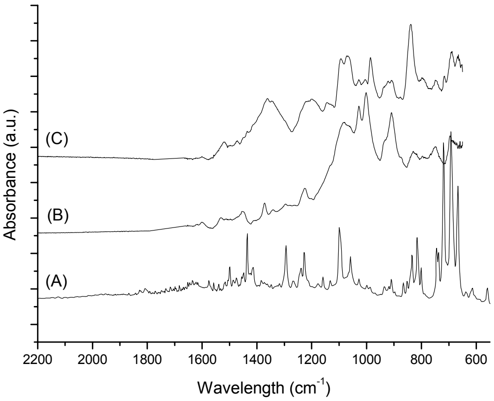

Figure 3. Infrared spectra of monomer (**1**) (A), PEDOT (B) and phosphole–EDOT copolymer (**3**) (C)

Composition of copolymer (**3**) was determined by energy dispersive X-ray spectroscopy (EDS) analysis from the experimental ratio of sulfur to phosphorus atoms in a dedoped film. The resulting copolymer composition was poly(1-phenyl (2,5-bis(2-thienyl)thioxophosphole)$_{0.14}$-co-3,4-ethylenedioxythiophene$_{0.86}$).

XPS measurements of copolymer (**3**) were carried out to investigate the surface composition of the new electrochromic material. When the XPS $P_{2p3/2}$ spectra of PEDOT and copolymer (**3**) were compared, a relative increase of phosphorus content was observed for this latter material as a consequence of the incorporation of (**1**) into the structure. The XPS S_{2p} spectra of PEDOT and copolymer (**3**) are illustrated in Figure 4. The S_{2p} spectrum for PEDOT shows the typical spin-split doublet, $S(p_{1/2,\ 3/2})$, with the well-known energy splitting of 1.2 eV. Han et al [49] assigned these peaks to sulfur atoms in neutral and positively charged EDOT units. So, the ratio of S^+/S_{Total} should give an indication of the doping level in PEDOT. In our case, the calculated doping level is $S^+/S_{Total} = 0.33$ (Figure 4A). This value is similar to the values reported by Han et al [49] and Zotti et al [50]. Figure 4B shows the XPS S_{2p} spectrum for copolymer (**3**). A tentative deconvolution of the main peak is illustrated including the presence of sulfur atoms from EDOT as well as sulfur atoms from thiophene rings and thiophosphole units of monomer (**1**).

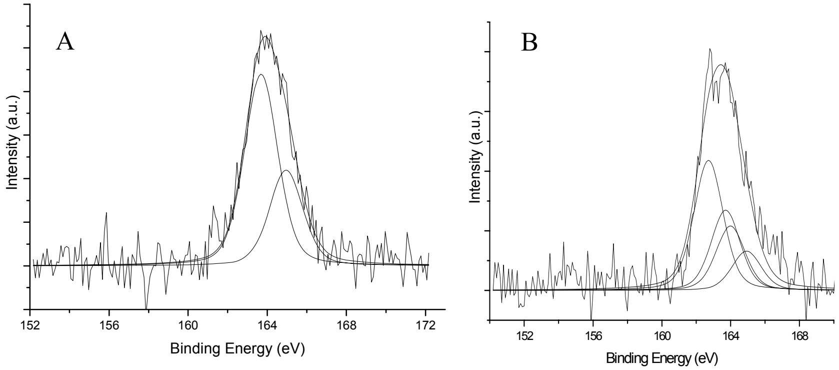

Figure 4. XPS S_{2p} spectra of PEDOT (A) and phosphole–EDOT copolymer (**3**) (B)

Thermal degradation behavior of conducting polymers is one of the most important characteristics for their potential applications. Figure 5 shows the high-resolution TGA curves for copolymer (**3**) and PEDOT. Figure 5A depicts thermal degradation of copolymer (**3**). This copolymer is stable until 175 ºC, where the weight loss is attributed to residual water or solvent (even when careful drying conditions where applied). From this temperature a continuous degradation takes place until major degradation happens in the region between 300-400 ºC. Thermal degradation of PEDOT (Figure 5B) presents a first degradation step which can be also attributed to loss of residual solvent or adsorbed water. This result is similar to that reported by Wei et al [48] and Choi et al [51]. The major decomposition occurs in the region between 150-500 ºC. Consequently, copolymer (**3**) is more stable than PEDOT up until 300 ºC and it again becomes more stable in the final part of the thermogram (above 450 ºC).

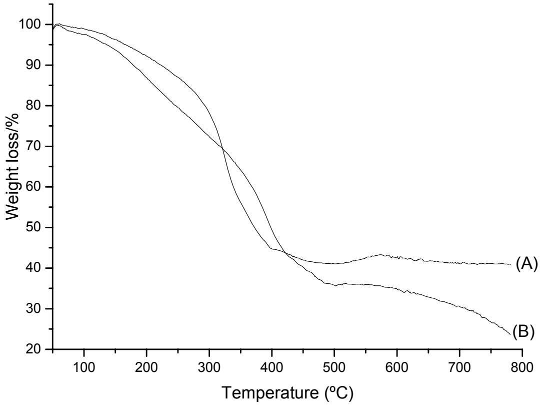

Figure 5. High-resolution TGA curves: phosphole–EDOT copolymer (**3**) (A) and PEDOT (B).

The UV/Visible/NIR spectra of copolymer (**3**) and poly(**2**), PEDOT, on ITO sheets is shown in Figure 6. Copolymer (**3**) exhibits an absorption maximum (715 nm) which is blue shifted compared to PEDOT ($\Delta\lambda_{max}$ = 135 nm) and red shifted compared to poly(**1**) ($\Delta\lambda_{max}$ = 200 nm). It is noteworthy that copolymer (**3**) presents a narrower optical band gap than poly(**1**) showing that incorporation of EDOT units favors the delocalization of the π-system. This effect can be attributed to the association of EDOT, an electron rich heterocycle, with 1-phenyl-2, 5-bis(thienyl)thiooxophosphole subunits, which are known to possess a low-lying LUMO, resulting in intramolecular charge transfer.

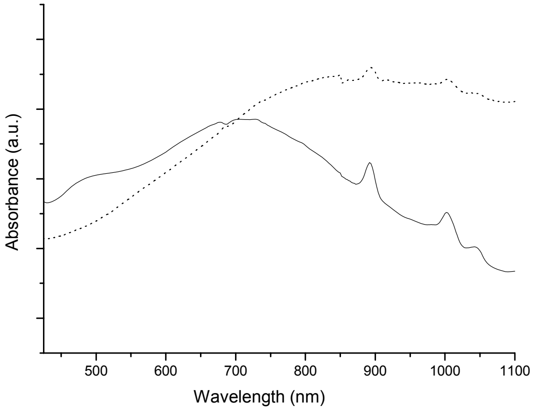

Figure 6. UV/Vis/NIR spectra of PEDOT (…………) and phosphole–EDOT copolymer (**3**)(——).

The E_g and λ_{max} for poly(**1**), poly(**2**) and copolymer (**3**) are summarized in Table 1.

Table 1. Band energy values and λ_{max} of poly(**1**), poly(**2**) and copolymer (**3**)

	Eg (eV)	λ_{max} (nm)
Poly(**1**)	1.7 [11]	515
Poly(**2**)	1.5-1.7 [54, 55]	850
Copolymer(**3**)	1.13*	715

*E_g value for copolymer (**3**) has been estimated with a λ_{onset} of 1100 nm from Figure 6.

The electrochromic properties of the phosphole–EDOT copolymer (**3**) have been studied for different film thickness by varying the number of scans in which electrodeposition takes place between 1 and 5 cycles. Figure 7 shows the evolution of the optical contrast vs. the number of cycles in both visible and near-IR region between +1.50 V and -1.40 V. The optical contrast for copolymer (**3**) is between 1.8 and 13 % in transmittance in the visible region (500 nm) and between 2.7 and 15 % in the near-IR region. The evolution of optical contrast with the number of cycles gives the optimum thickness of copolymer (**3**) to achieve the maximum optical contrast which is about 2 - 3 cycles in the visible region and 5 cycles in the NIR region.

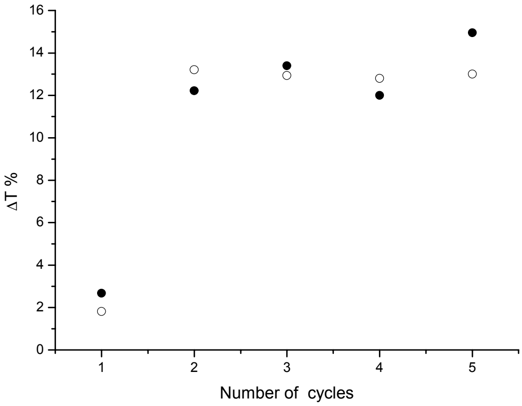

Figure 7. Optical contrast as a function of the thickness for electrochromic phosphole–EDOT copolymer (**3**) electrochemically deposited over plastic ITO sheets: (○) visible region and (●) near-IR region

The kinetics of the electrochromic behavior of copolymer (**3**) was determined using chronoamperometric methods between -1.4 V and +1.5 V vs. Ag/AgCl at a constant wavelength of 500 nm. Quantification of switching time was made by defining a change in 90 % of the total absorbance span. The optical response is 5 s for coloring to black (reduction process) and 3 s for coloring to blue (oxidation process). Switching time in the range from 1 to 5 s for coloration and bleaching are normal for electrochromic polymers [54].

Figure 8 shows the optical absorption spectra for the phosphole–EDOT copolymer (**3**) at different doping levels between -1.4 V and +1.5 V. At -1.4 V a band exists at 429 nm corresponding to the polymer. The intensity of this band was decreasing upon oxidation leading to the disappearance of such a band at -0.5 V. A new band emerges at 575 nm at -1.0 V corresponding to the copolymer structure in the doped state which moved to 675 nm when the potential was increased.

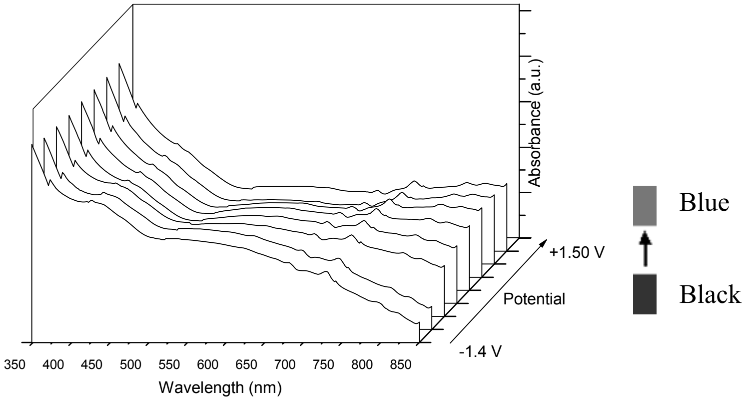

Figure 8. Spectroelectrochemical spectra for electrochromic phosphole–EDOT copolymer (**3**) grown on an ITO plastic substrate.

Finally, Figure 9 depicts AFM images for PEDOT and copolymer (**3**). Important morphologic differences are observed even when in both cases the observed particles are spherical and aggregated. The spherical shape of the particles present in the films is common in thin films of conducting polymers [55]. In the case of PEDOT, Figure 9A, the observed particles have a diameter between 200-300 nm giving an average roughness of 150 nm. For copolymer (**3**), Figure 9B, spherical particles with a diameter between 100-250 nm are found with a RMS roughness of 123 nm. Consequently, copolymerization of both monomers leads to the formation of smaller particles and a smoother surface.

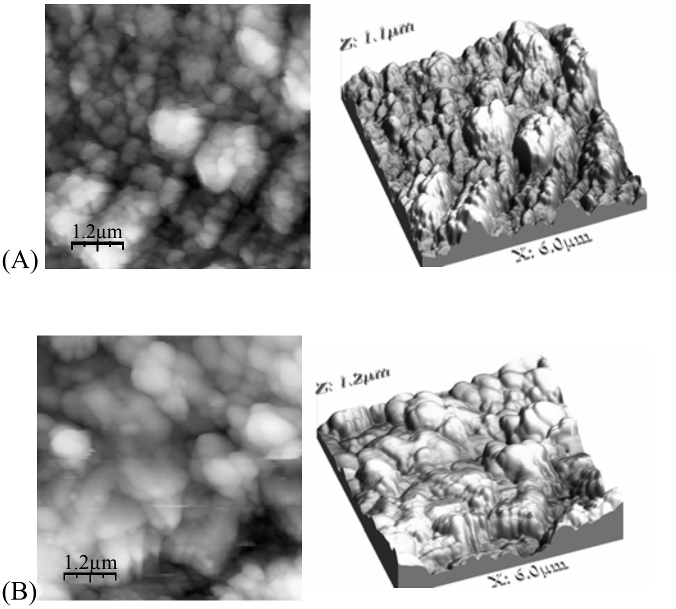

Figure 9. AFM morphology of PEDOT (A) and phosphole–EDOT copolymer (**3**) (B).

Conclusions

An electrochromic copolymer containing phosphole and EDOT units, poly(1-phenyl-2,5-bis(2-thienyl)thioxophosphole-co-3,4-ethylendioxythiophene), with a 1-phenyl-2,5-bis(2-thienyl)thioxophosphole content of 14 mol % was synthesized by cyclic voltammetry. The copolymer structure was investigated by FTIR and EDS spectroscopy as well as XPS measurements. TGA results pointed to an increased thermal stability of the copolymer when compared to neat PEDOT. The copolymer showed an oxidation potential of 0.6 V, lower than that of the corresponding phosphole homopolymer (1.3 V vs Ag/AgCl) but higher than that of PEDOT (0.16 V vs Ag/AgCl). As a result of intramolecular charge transfer in the copolymer a narrower optical band gap was found when compared to the corresponding phosphole homopolymer. The copolymer exhibited an UV/Vis/NIR absorption maximum at 715 nm and displayed blue-to-black electrochromic behavior with a maximum optical contrast of 13 % in the visible region and 15 % in the NIR region. AFM measurements depicted a morphology comprising aggregated nanoparticles of 100–250 nm in size and a RMS roughness of 123 nm, smaller than that observed for PEDOT. In summary, this work opens the way for the synthesis of other electrochromic phosphole derivative-EDOT copolymers which are useful for electrooptical applications

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