A Processable Green Polymeric Electrochromic

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ABSTRACT: We report electrochemical and optical properties of the first electrochemically and chemically prepared green, soluble conducting polymer in its neutral form. Oxidative electrochemical and chemical polymerization of dioctyl-substituted 2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-*b*]pyrazine (**3b**) results in a soluble polymer (**4b)** with novel optical properties. The neutral polymer **4b** absorbs both blue (above 600 nm) and red light (below 500 nm), reflecting a saturated green color. In the oxidized form, these absorptions are depleted, resulting in a transmissive pale brown polymer with very strong absorption in the near-infrared. Electrochemical and spectroelectrochemical semiconductor band gaps of **4b** were found to be ca. 1.3 eV. Molecular weight analysis showed that soluble polymers have different conjugation length from oligomers to polymers. Since the monomer **3b** has low oxidation potential (0.48 V vs Ag/Ag^+), mild oxidizing agents (i.e., $CuCl_2$) initiate chemical polymerization. The oxidant/monomer ratio should be at least 3:1 to get a desired green polymer. High green color saturation as well as the high solubility in common organic solvents makes this polymer a promising material to bring polymeric electrochromics closer to red, green, and blue (RGB) realization.

Introduction

Since the discovery of the first conducting polymer (CP),[1] many researchers have focused on processable conducting polymers which are of particular importance for industrial applications.[2] Conductive coatings of electroactive polymers have been obtained via different routes such as using polyanion-like polyelectrolytes[3−5] as dopant or by functionalization of the monomer by introducing an alkyl side chain.[6] The presence of alkyl side chains not only allows an easier processing of some electroactive polymers but also modulates the electronic properties of the conjugated main chain.[7] For example, several groups have reported that a decrease in the oxidation potential of the polymer with a better stability in the oxidized state was achieved by introduction of strong electron-donating alkoxy side chains.[8−12] In addition, the presence of alkoxy side chains decreases the steric hindrance in the immediate vicinity of the main chain, resulting in planar, highly conjugated structures with a lower band gap. On the other hand, the presence of flexible side chains and the counterions can significantly change the stability of the oxidized polymer.[13,14] The repulsive interactions between the flexible side chains and the counterions may be responsible for the poor stability of some of these doped conducting polymers, especially at high temperatures. To overcome this problem, ionic side chains (sulfonates, carboxylates, phosphonates, etc.) can be covalently bonded to the conjugated polymer backbone, resulting in a water-soluble and self-dopable conducting polymer.[7,15,16]

The ability of a reversible change in the reflected or transmitted light upon electrochemical oxidation or reduction of electrochromic materials has aroused the interest of scientists over the past three decades.[17,18] Electrochromic properties have proved especially useful or promising for the construction of mirrors,[19] displays,[20−22] windows,[23−27] and earth-tone chameleon materials.[28−30] On the basis of this concept, electrochromic rear-view and side-view mirrors have been recently commercialized in the automotive industry.[31,32]

During the development of electrochromic polymers in the past three decades, polymers absorbing/reflecting blue and red lights in their neutral states were mainly studied. Since absorption at only one dominant wavelength is required to obtain blue or red, these can be obtained relatively easily by tuning the CP's band gap. The missing third leg (green) of color space, which was recently disclosed by our group,[33] was an important barricade to surmount in order to achieve commercialization of polymeric electrochromics.[34] At least two simultaneous absorption bands (red and blue) are required to observe a green light. While these chromophores absorb red and blue light in the neutral form of the polymer, they should also deplete together when the polymer is oxidized. Now, except for the fact that depletion does not produce a clear film, these properties are in hand with the polymer films obtained from successful electropolymerization of 2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-*b*]pyrazine (DDTP).[33] Obviously, the next step should be a soluble version of the green polymer. Herein we present the first report of electrochemical, chemical, and optical properties of an electrochemically or chemically prepared soluble, green, neutral conjugated polymer.

Results and Discussion

Electrochemical and Chemical Polymerization. As expected, dioctyl substitution of DDTP results in a more soluble monomer, 5,7-bis(3-octylthiophen-2-yl)-2,3-dithiophen-3-yl-thieno[3,4-b]pyrazine (**3b**), and should give a soluble polymer (Figure 1). Monomer **3b** was electrochemically or chemically polymerized to give polymer **4b**. Electrochemical polymerization was achieved potentiostatically at +0.500 V vs Ag/Ag^+ or potentiodynamically between −0.800 and +0.525 V vs Ag/Ag^+ in a mixture of dichloromethane (DCM) and acetonitrile

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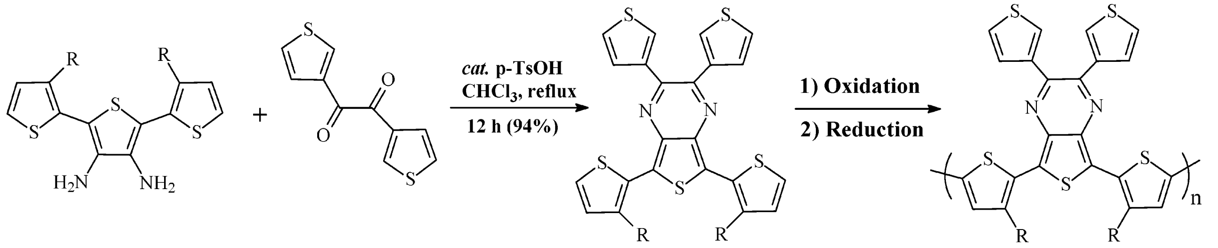

1a R:H
1b R: Octyl

2

3a R: H
3b R: Octyl

4a R: H
4b R: Octyl

Figure 1. Synthesis of dioctyl-substituted 2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-*b*]pyrazine monomer and its polymer. Oxidation and reduction processes for polymerization can be achieved electrochemically or chemically. In the case of chemical polymerization of **3**, $FeCl_3$ or $CuCl_2$ and 30% ammonium hydroxide were used for oxidation and reduction (dedoping), respectively.

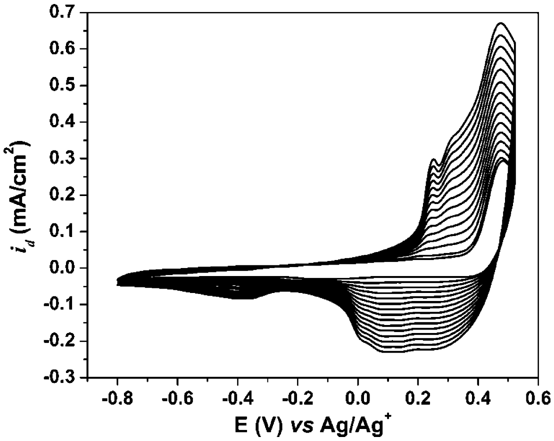

Figure 2. Oxidative electropolymerization of **3b** in a mixture of DCM and MeCN (20/80, v/v) solution containing 10^{-2} M monomer and 0.1 M Bu_4NPF_6.

(MeCN) (20/80, v/v) solution containing 10^{-2} M monomer and 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (Figure 2). Since **3b** was very soluble in DCM and insoluble in MeCN, an appropriate mixture of these solvents was used for electrochemical polymerization to deposit polymer films on the electrode. This high solubility of the polymer in DCM precluded its isolation when polymerized electrochemically.

During the electrochemical polymerization, an irreversible oxidation of the monomer **3** appeared in the first cycle at +0.480 V vs Ag/Ag$^+$, followed by very fast deposition on subsequent cycles, due to the redox system that grows rapidly at potentials lower than the monomer oxidation. The character of electrochemical polymerization of **3b** is slightly different from **3a**.[33] For instance, the oxidation of **3b** is 20 mV lower than **3a**, yet polymer growth appears at higher potentials in this case.

A typical chemical polymerization of **3b** was achieved using copper(II) chloride, iron(III) chloride, and ceric(IV) ammonium nitrate (CAN) oxidants (Figure 1). The dark oxidized polymer was first washed with methanol, reduced with 30% ammonium hydroxide, and dried under vacuum. The neutral polymer **4b** was isolated as a saturated green powder. The polymer products obtained using these oxidizing agents show different character. As the monomer was oxidized with higher oxidation potential oxidizing agents (i.e., CAN), instead of a green polymer a purple, insoluble polymer was obtained. It should be noted that a purple color does not have a single dominant wavelength located on the spectral locus of the CIE 1931 (CIE: Commission Internationale de l'Eclairage) diagram and results from the addition of several absorptions located at different wavelengths in the visible spectrum.[35] This may stem from the oxidation of two pendant thiophenes at the same time with terthiophene, resulting in a cross-linked, insoluble polymer. Similar cross-linked polymers were also observed during electrochemical polymerization of dialkyl-unsubstituted monomer at high potentials.[33] Mild oxidizing agents (i.e., $CuCl_2$) give better results for the polymerization of **3b** because of its lower oxidation potential.

Electrochemistry. Cyclic voltammetry (CV) of electrochemically and chemically prepared polymers upon p-doping revealed two stable redox waves. Figure 3 presents comparison of the corresponding CVs of **4b** at the scan rates of 50, 100, 150, and 200 mV/s in the solid state and in solution. Very well-defined redox processes ($E_{1/2}$) at +0.19 and +0.26 V vs Ag/Ag$^+$ were observed for electrochemically prepared **4b**. These waves were extremely stable, and although they were very close to each other (i.e., the difference between peak potentials for the oxidation is less than 50 mV), they did not interfere at high scan rates as high as 500 mV (Figure 3A, inset). The shift in the peak potentials as the scan rate was increased from 50 to 500 mV were less than 30 and 10 mV for p-doping and dedoping, respectively. Chemically prepared polymer's CV shows slightly different character from the CV of electrochemically prepared polymer. Although both peaks can clearly be seen, they are not as sharp as electrochemically prepared **4b**, and the difference between peak potentials for the oxidation is about 130 mV (Figure 3B). A better CV for electrochemically prepared **4b** may stem from the lower molecular weight and a better order of the polymer on the electrode surface during polymerization that allows easier movement of counterions inside and outside of the polymer. The peaks are even broader for the CV of the polymer in solution because of its very low concentration near the electrode (Figure 3C). It is important to note that the redox potentials appear at almost the same place for the polymer's CV in three different conditions.

Since the pyrazine bridge between thiophene rings is an electron-accepting group, **4b** is also an n-dopable polymer. Figure 4 presents the CV of **4b** upon p- and n-doping at different conditions. The CV of polymer **4b** shows very similar phenomena with the p-doping presented above. For example, peaks in the CV of electrochemically prepared polymer are better defined, and peak separation in the chemically prepared polymer is slightly higher. The only difference is the slight positive shifts on the redox potentials in the CV of **4b** in solution

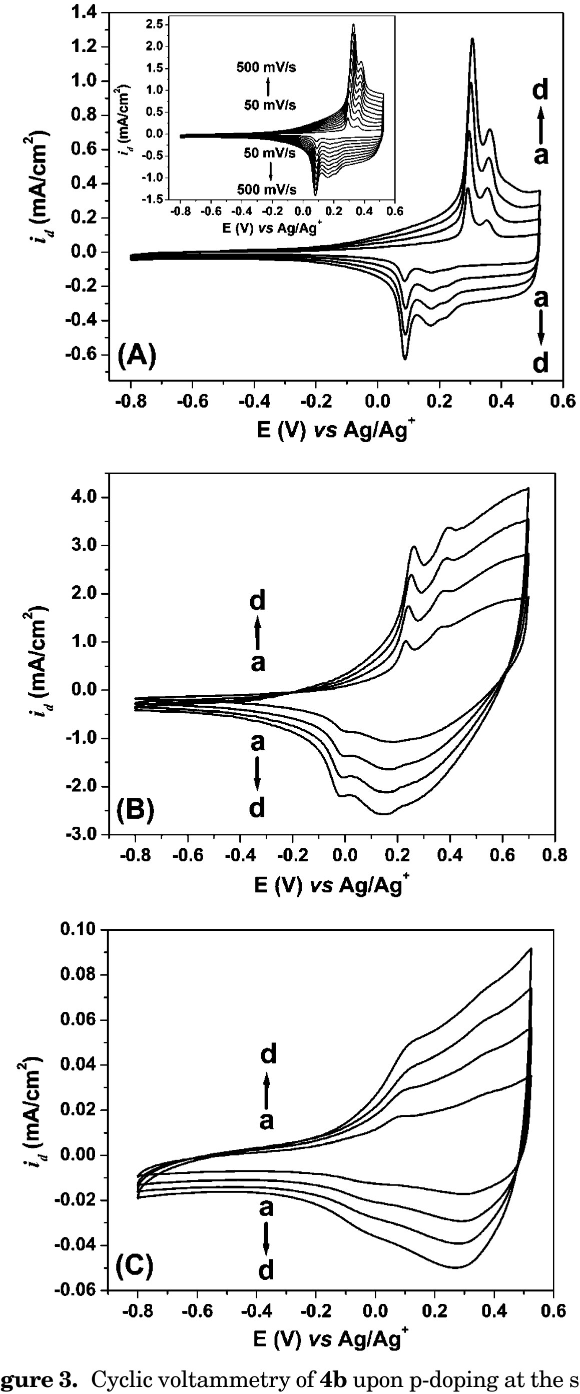

Figure 3. Cyclic voltammetry of **4b** upon p-doping at the scan rates (a) 50, (b) 100, (c) 150, and (d) 200 mV/s: (A) **4b** was prepared potentiodynamically from a solution of DCM:MeCN mixture (20:80) containing 0.1 M Bu_4NPF_6 and cycled in 0.1 M Bu_4NPF_6/MeCN (inset: different scan rates from 50 to 500 mV/s); (B) chemically prepared **4b** was drop-cast on Pt button electrode and cycled in 0.1 M Bu_4NPF_6/MeCN; (C) chemically prepared **4b** was dissolved in 0.1 M Bu_4NPF_6/DCM and cycled in the same solution.

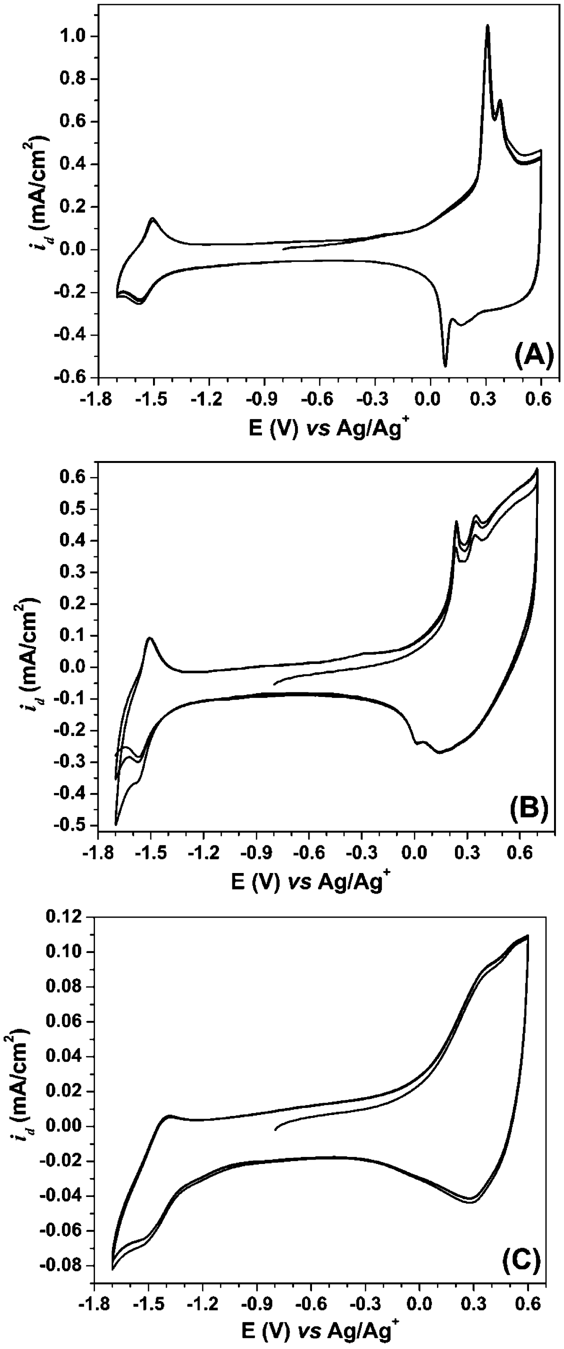

Figure 4. Cyclic voltammetry of the polymer **4b** upon p- and n-dopings at a scan rate of 200 mV/s: (A) polymer **4b** was prepared potentiodynamically from a solution of DCM:MeCN mixture (20:80) containing 0.1 M Bu_4NPF_6 and cycled in 0.1 M Bu_4NPF_6/MeCN; (B) chemically prepared **4b** was drop-casted on Pt button electrode and cycled in 0.1 M Bu_4NPF_6/MeCN; (C) chemically prepared **4b** was dissolved in 0.1 M Bu_4NPF_6/DCM and cycled in the same solution.

(Figure 4C). Polymer **4b** presents reduction waves ($E_{1/2}$), corresponding to the n-dopings, at -1.54 and -1.46 V vs Ag/Ag$^+$ in the solid state and in the solution, respectively. It should be noted that there is a slight difference between the amounts of transferred electrons during the redox processes upon p- and n-doping. Higher peak currents were obtained at the p-side of doping compared to n-side, reflecting that the polymer is a better electron donor than acceptor. The band gap (E_g) calculated from the onset potentials of p- and n-doping of **4b** is 1.33 eV for three measurements. This value is slightly higher (0.18 eV) than the E_g of the unsubstituted polymer.[33]

Spectroelectrochemistry. The presence of alkyl side chains not only allows an easier processing of electroactive polymers but also modulates the electronic properties of the conjugated main chain.[7] Interestingly, spectroelectrochemistry of both alkyl substituted and unsubstituted polymers shows almost the same spectrum and color saturation. The same band gap was also obtained from electrochemistry and spectroelectrochem-

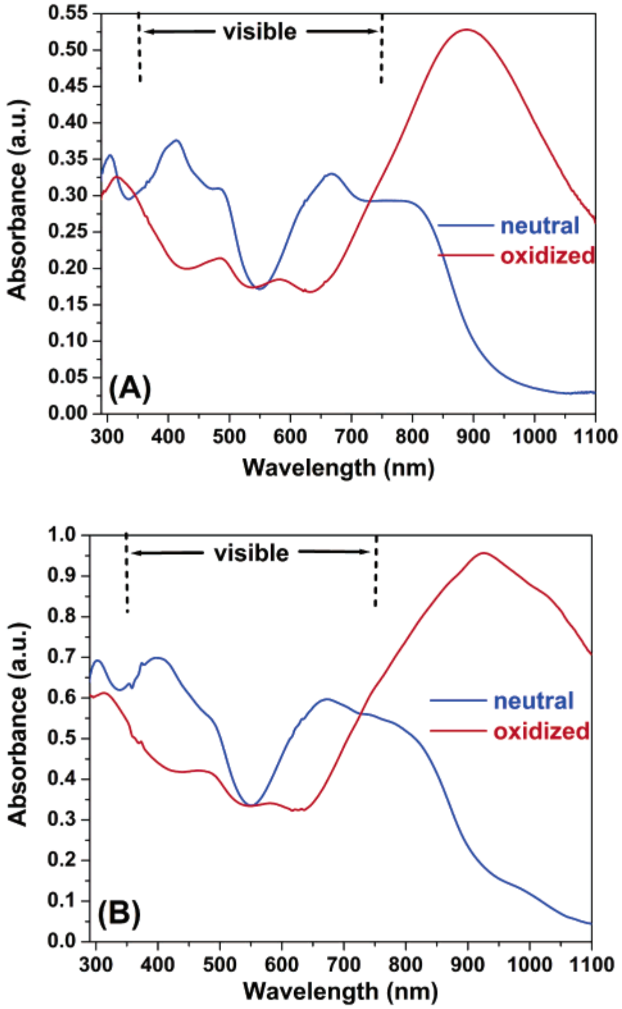

Figure 5. In-situ spectroelectrochemistry of (A) electrochemically and (B) chemically prepared **4b** on ITO-coated glass slides in 0.1 M Bu_4NPF_6/MeCN at the neutral and oxidized states.

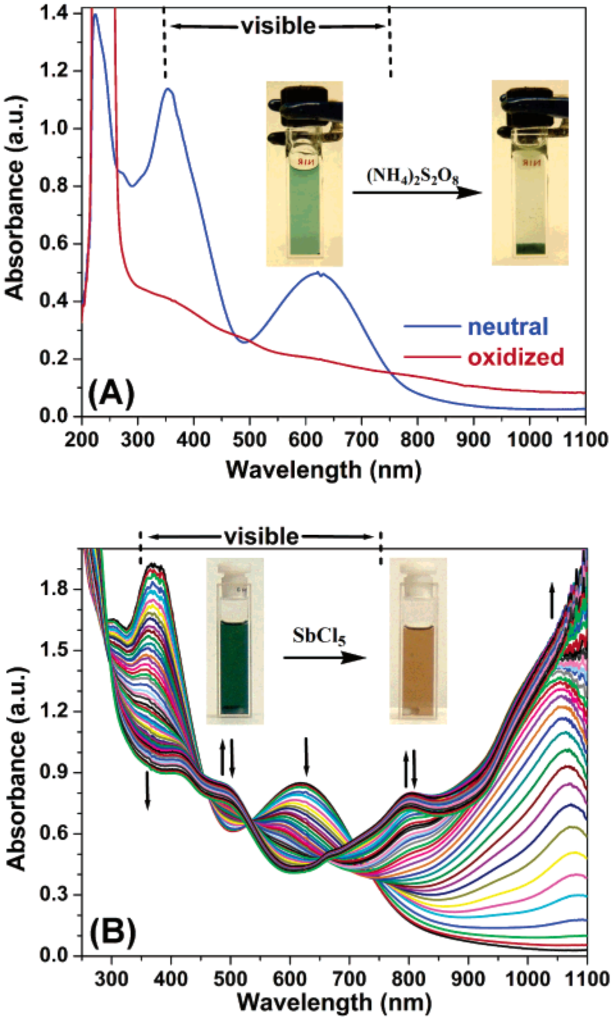

Figure 6. (A) Neutral and oxidized spectra of chemically prepared **4b** in THF. For oxidation $(NH_4)_2S_2O_8$ was used. (B) Stepwise solution oxidation of polymer **4b** with increasing $SbCl_5$ concentration in DCM. The insets show photographs of the neutral and doped form of polymer solution.

istry in the solid state. More interestingly, polymers synthesized by different methods (i.e., using different oxidizing agents and electrochemistry) showed similar properties. Switching properties of electrochemically and chemically prepared polymers are compared in Figure 5. For spectroelectrochemical switching, thin polymer films of **4b** were deposited on ITO-coated (ITO is indium tin oxide) slides in two ways: In the first, polymer films were prepared potentiodynamically as explained before. In the second, polymer **4b** was prepared by chemical oxidation with $CuCl_2$, and then a concentrated solution of **4b** in DCM was prepared and spin-cast on an ITO-coated slide. Then, in both cases, polymer films were electrochemically switched between their oxidized and neutral states in 0.1 M Bu_4NPF_6/MeCN, and their spectra were recorded in situ. Parts A and B of Figure 5 show electrochemically and chemically prepared polymers' spectra, respectively. An almost identical spectrum was obtained for both polymers. For the neutral polymer, two main absorptions were observed in the visible region at 410 and 670 nm with shoulders at 485 and 790 nm. As polymer films were oxidized, all absorptions in the visible were depleted at the expense of a strong absorption in the near-infrared (NIR) region at ca. 900 nm. The band gap calculated from the onset of the $\pi-\pi^*$ transition is 1.3 eV for both electrochemically and chemically prepared polymer films, in good agreement with the value determined from electrochemistry.

Solution Doping. For spectrochemical switching, chemically prepared **4b** was switched in solution using ammonium persulfate (APS) and antimony(V) chloride (APC) as oxidizing agents. Figure 6A depicts the optical spectra of neutral and oxidized (with APS) polymer solution of **4b** in THF. The spectrum of neutral polymer in solution is slightly different from that in the solid state. Since the main absorptions shift to shorter wavelengths, namely 355 and 620 nm with a valley at 485 nm, polymer solution results in another tone of green. When the polymer solution was oxidized with APS, first, a dark green polymer was immediately precipitated. After several hours, the precipitate changed its color from dark green to white. The absorptions in the visible were immediately depleted after the addition of several drops of oxidant solution. A solution of **4b** in DCM was oxidatively doped by stepwise addition of 5 μL aliquots of 10^{-5} M solution of APC in DCM. The results are presented in Figure 6B. As can be seen from the initial spectrum, the neutral polymer **4b** in DCM has two absorption maxima at 365 and 620 nm. Comparing the maximum absorptions of the neutral polymer

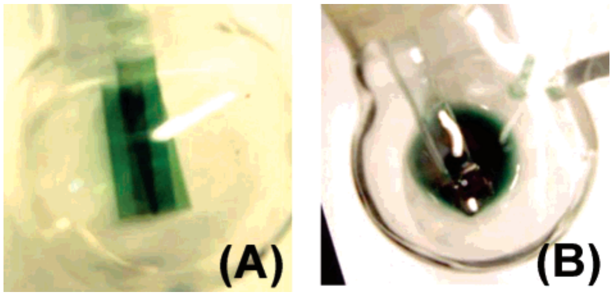

Figure 7. Pictures of (A) polymer **4b** coated of ITO-coated slides and (B) after dissolving the polymer in d_2-tetrachloroethane in a round-bottom flask.

in the solution and the solid state, the main absorptions in the visible region responsible for its color appear at 40−50 nm longer wavelengths in the solid state. This may stem from a better $\pi-\pi$ stacking in the solid state. As a result of the shift in the $\pi-\pi^*$ transitions, a slight increase (0.2 eV) in the band gap was observed. Upon successive additions of APC, the $\pi-\pi^*$ transitions were depleted at the expense of four lower energy transitions at 500, 800, and 1070 nm and in the NIR region. At the initial steps of oxidation, an increase in the intensities of the absorptions at 500 and 1070 nm was observed with the depletion of the absorptions at 365 and 620 nm. Upon further oxidation, the absorption at 500 nm started to decrease at the expense of a new absorption at 800 nm, which also decreased in the later steps of oxidation to produce a stronger absorption at longer wavelengths than 1100 nm. Interestingly, there are four isosbestic points at 285, 455, 535, and 720 nm, which were less-defined in the solid-state spectroelectrochemistry, as a result of possible trapped charges in the polymer backbone.

Solubility and Structural Characterization. Electrochemically prepared polymer films of **4b** on ITO-coated glass slides were dedoped electrochemically in monomer free-electrolyte solution and dissolved in d_2-tetrachloroethane. Figure 7 presents photographs of polymer-coated ITO-coated slides before and after dissolving **4b** in d_2-tetrachloroethane in a round-bottom flask. ^{1}H NMR spectroscopy of the resulting polymer demonstrated that protons on the α- and α′-positions of the pendant thiophene rings (at the 2- and 3-positions of the pyrazine ring) remained intact after electrochemical polymerization, confirming the proposed structure for polymer **4b** in Figure 1.

Molecular weight analyses were carried out using matrix-assisted laser desorption ionization mass spectrometry (MALDI−MS) and gel permeation chromatography (GPC) (polystyrene standards) with THF as the mobile phase. Since we decided to use milder oxidizing agents for the synthesis of **4b**, $CuCl_2$ was selected as an oxidant for a detailed investigation of the effect of oxidant/monomer ratio on the resulting polymer. While there was a drastic change in the molecular weight as the ratio of oxidant/monomer was increased from 1 to 5, a slight decrease was observed in the yield of soluble polymer. The yield decreased from essentially quantitative to 85% as the oxidant/monomer ratio increased from 1 to 5. Three main fractions were observed in the GPC spectrum for different combinations of oxidant/monomer ratios. Figure 8 presents a GPC trace of **4b** prepared using oxidant/monomer ratios of 1:1 and 5:1. We followed the changes with the intensity of the three peaks labeled a, b, and c in Figure 8, and results obtained from the ratio of these peaks vs oxidant/monomer ratio are presented in the inset of Figure 8. As expected, when the oxidant/monomer ratio was increased, an increase in molecular weight of the polymer was observed. For example, when the oxidant/monomer ratio was 1:1, the ratios of a and b to c were 0.13 and 0.28, respectively, indicating that polymers were mostly low molecular weight. When the oxidant/monomer ratio was increased to 5:1, these ratios increased to 2.30 and 2.90, respectively, indicating that most of the polymers had lower retention time. From these results it can be concluded that as the oxidant/monomer ratio was increased by 5 times, the average molecular weight of resulting polymer increased more than 10 times. It should be noted that the same period of time was used for oxidative polymerization with different oxidant/monomer ratios. As the polymerization time was extended, a slight increase in molecular weight could be observed for all ratios.

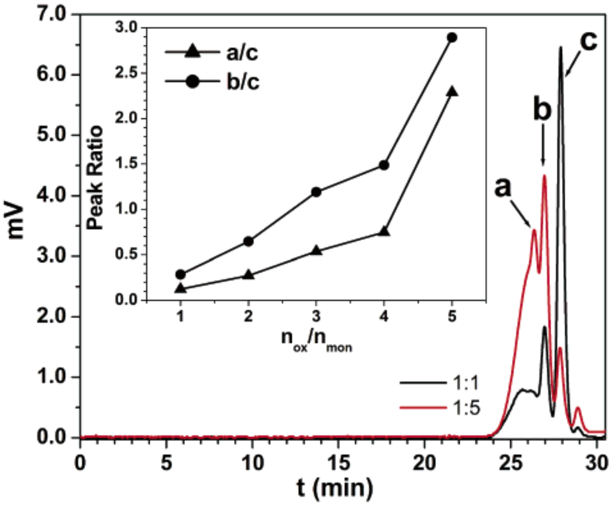

Figure 8. Gel permeation chromatography (GPC) of polymer **4b**. GPC was performed on 2 mg/mL THF solutions of **4b**. Inset figure shows the molecular weight behavior of polymer **4b** as a function of oxidant to monomer mol ratio. The labels a, b, and c correspond to the three main peaks observed during the GPC measurements at the elution time of 26, 27, and 28 min, respectively.

MALDI-MS studies were also performed on **4b,** and as an example, the spectrum of the polymer which was prepared using an oxidant/monomer ratio of 3 is given in Figure 9. The occurrence of the most intense peaks is ca. 687 g/mol, a mass corresponding to the polymer repeat unit. The maximum peak that we could count corresponds to 14 repeating units of monomer that contains 42 thiophene units on the polymer backbone. If the saturation length for optical absorption of oligothiophenes is about 9−14 repeating units,[36] then the number of thiophenes determined is sufficient to obtain desired properties for the use of this polymer as a polymeric electrochromic.

The effect of oxidant/monomer ratio on the resulting polymer was also studied by UV−vis spectroscopy. Figure 10 shows the UV−vis spectrum of 5×10^{-5} M polymer solution in THF and the change in the peak maximum at the red and blue region of visible. The UV−vis absorption of the THF solution of **3b** as well as the neutral polymer **4b** presents two main peaks in the visible region (Figure 10A). As the oxidant/monomer ratio for polymerization was increased, a red shift was observed in the maximum of both absorptions. This

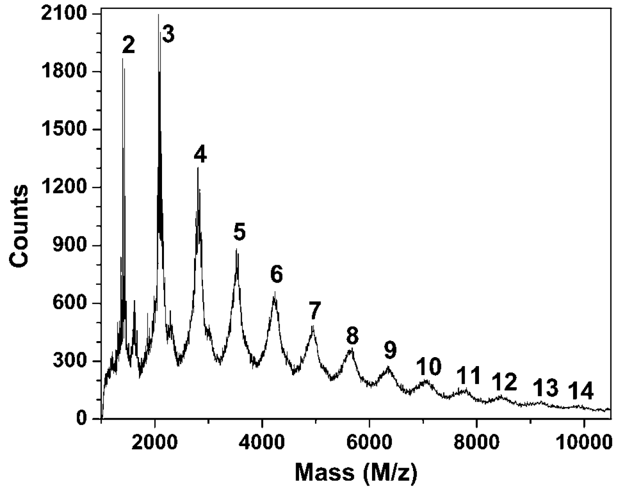

Figure 9. Matrix-assisted laser desorption mass spectral analysis of polymer **4b** prepared chemically using an oxidant/monomer ratio of 3.

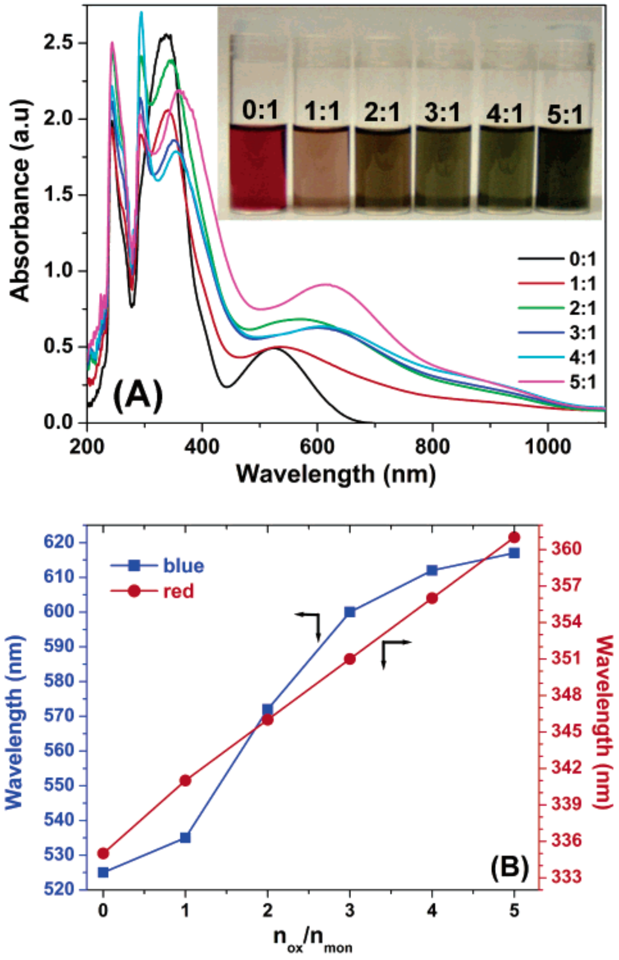

Figure 10. (A) Absorption spectrum of 5×10^{-5} M **4b** in THF. Polymers were prepared chemically using different mol ratio of oxidant to monomer. (B) Oxidant/monomer ratio dependence of the absorption maximum (λ_{max}) of polymer **4b** at the blue and red regions of the visible spectrum.

result is in a good agreement with the results obtained from GPC because it is well-known that absorption of the π−π* transitions of conducting polymers shifts to the longer wavelengths as the conjugation length increases, in other words, as the molecular weight increases.[37,38] The wavelength shift in the low-energy band decreases in each step as the oxidant/monomer ratio increases (Figure 10B). When the oxidant/monomer ratio was increased from 1 to 5, shifts in the λ_{max} of 20 and 80 nm were observed for the red and blue absorptions, respectively. The main change in the λ_{max} of the blue absorption can be concluded as the polymerization proceeds via terthiophene part of the monomer as it was explained in our previous work.[33] A 20 nm shift in the red absorption may stem from the side effect of the shift in the blue absorption. The color of neutral polymer changes its color from pale reddish-pink to dark green as the ratio of oxidant to monomer was increased from 1 to 5 (Figure 10A, inset). A desired green color of polymer solution was reached at the mole ratio of 3:1.

Conclusions

In conclusion, the first soluble neutral green, conjugated polymer was synthesized. The oxidative electrochemical and chemical polymerization of **3b** results in soluble **4b** with novel optical properties. The neutral polymer **4b** absorbs blue (above 600 nm) and red colors (below 500 nm), reflecting a saturated green color. In the oxidized form, these absorptions are depleted resulting in a transmissive pale brown color with very strong absorption in near-infrared region. The band gap of the polymer was found to be ca. 1.3 eV from both electrochemistry and spectroelectrochemistry. Molecular weight approximations showed that soluble polymer samples have sufficient conjugation length for the desired properties. Because of the low oxidation potential of monomer **3b** (0.48 V vs Ag/Ag$^+$), only mild oxidizing agents are required for chemical polymerization. The oxidant/monomer ratio should be at least 3:1 to get a desired green polymer. High green color saturation as well as the high solubility in common organic solvents makes this polymer a promising material to bring polymeric electrochromics closer to RGB realization.

Experimental Section

All chemicals were purchased from Aldrich Chemical. Propylene carbonate (PC) (99.7%, anhydrous), dichloromethane (DCM), tetrahydrofuran (THF), and acetonitrile (MeCN) were distilled over calcium hydride before use.

All reactions were performed under argon or glovebox unless mentioned in the procedure. The products were put under high vacuum overnight after flash chromatography. NMR studies were carried out on Bruker Avance-500 or Avance-600 spectrometers. Tetramethylsilane (TMS) was used as the internal standard for ^{1}H NMR, and the deuterated solvent ($CDCl_3$) was used as a standard for ^{13}C NMR. FT-IR spectra were recorded on a Mattson Infinity IIa spectrometer with a DRIFT accessory from PIKE Technologies, on a diamond frit. High-resolution mass spectra (HRMS) were obtained by a VG ZAB-SE mass spectrometer with EI source. Column chromatography was performed on silica gel 230−400 mesh (flash) from E. Merck or from Scientific Absorbents; thin-layer chromatography (TLC) was performed on glass plates coated with silica gel $^{60}F_{254}$ from E. Merck.

High-resolution MALDI−TOF mass spectra were obtained by an Applied Biosystem DE-STR MALDI−TOF mass spectrometer. The matrix used for MALDI−TOF MS was terthiophene.

Molecular weights were also determined by gel permeation chromatography (GPC) using a Waters 600 controller, a Waters 410 differential refractometer, and a Viscotek T50 differential viscometer. Samples were filtered through a Gelman 0.2 μm PTFE filter membrane prior to injection. Three 300 mm PLgel 10 μm MIXED-B columns were calibrated with polystyrene standards using THF as the eluent with a flow rate of 1.0 mL/min.

Electropolymerization was carried out with a BAS 100B/W potentiostat, employing a platinum button (diameter: 1.6 mm; area 0.02 cm^2) or ITO-coated glass slides as working electrode, a platinum flag or wire as counter electrode, and a silver wire or 0.01 M $Ag/AgNO_3$ (Ag/Ag^+) as reference. The electrolyte used was 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in DCM, MeCN, or a mixture of MeCN and DCM. The electrodeposition was performed from a 0.01 M solution of the monomer in the electrolyte potentiodynamically at a scan rate of 20 mV/s or potentiostatically at 50 mV above the oxidation potential of monomer. Cyclic voltammetry was carried out using the same electrode setup using monomer-free electrolyte solution.

Spectroelectrochemical data were recorded on a Hewlett-Packard 8453 UV−vis spectrophotometer connected to a computer. A three-electrode cell assembly was used where the working electrode was an ITO-coated glass slide (7 × 50 × 0.6 mm, $R_s \leq 10\ \Omega/\square$, Delta Technologies Inc.), the counter electrode was a platinum wire, and a Ag wire was used as pseudo-reference electrode. The pseudo-reference was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc^+) in the electrolyte ($E_{1/2}(Fc/Fc^+) = +0.130$ V vs Ag wire and +0.080 V vs Ag/Ag^+ in 0.1 M Bu_4NPF_6/MeCN). The potentials are reported vs Ag/Ag^+. Polymer films for spectroelectrochemistry were prepared by potentiodynamic deposition or spin-coating on ITO-coated glass slides.

A Fujifilm (FinePix A303) digital camera was used to take photographs of the polymers at high resolution.

Oxidative polymerization of monomer, 5,7-bis(3-octylthiophen-2-yl)-2,3-dithiophen-3-yl-thieno[3,4-*b*]pyrazine (**3b**), was achieved by using different oxidizing agents with different oxidation power (i.e., ceric(IV) ammonium nitrate, ferric(III) chloride, and copper(II) chloride).[39] Monomer (10^{-2} M) and oxidizing agents were dissolved in DCM (3 mL) and MeCN (1 mL), respectively. Different ratios of copper(II) chloride to the monomer (from 1 to 5) were used. The solution immediately turned dark black-blue in color. The polymerization was allowed to stir for 15 h at room temperature. The oxidized polymer was first washed with 10 mL of methanol (5 times) to remove excess oxidant and then reduced with 30% ammonium hydroxide by washing for 5 min (three times), followed by drying under vacuum. The neutral polymer has a very saturated green color. Yield 80−95%. IR (drift) v: 2955, 2920, 2853, 1600, 1470, 1427, 1361, 1262, 1185, 1100, 1050, 800 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 0.88 ($-CH_3$), 1.26 ($-CH_2$), 1.39 ($-CH_2$), 1.52 ($-CH_2$), 2.97 ($-CH_2$), 7.07, 7.23, 7.36 (2-position of end group of polymer backbone), 7.44 (5-position of pendant thiophenes), 7.58 (2-positions of pendant thiophenes). The intensity of the 7.36 ppm resonance is indicative of the relatively low molecular weight of the oligomer.

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References and Notes

(1) Shirakawa, H.; Lewis, E. J.; McDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.
(2) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1998.
(3) Jonas, F.; Kraft, W. US Patent No. 5 300 575, 1994.
(4) Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R *Adv. Mater.* **2000**, *12*, 481.
(5) Sarac, A. S.; Sonmez, G.; Ustamehmetoglu, B.; Mustafaev, M. I. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1255.
(6) Yoshino, K.; Love, P.; Onoda, M.; Sugimoto, R. *Jpn. J. Appl. Phys., Part 2: Lett.* **1988**, *27*, L2388.
(7) Sonmez, G.; Schwendeman, I.; Schottland, P.; Zong, K.; Reynolds, J. R. *Macromolecules* **2003**, *36*, 639.
(8) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.
(9) Faid, K.; Cloutier, R.; Leclerc, M. *Macromolecules* **1993**, *23*, 2501.
(10) Hong, Y.; Miller, L. L. *Chem. Mater.* **1995**, *7*, 1999.
(11) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.
(12) Havinga, E. E.; Mutsaers, C. M. J.; Jenneskens, L. W. *Chem. Mater.* **1996**, *8*, 769.
(13) Inganas, O. *Trends Polym. Sci.* **1994**, *2*, 189.
(14) Hanna, R.; Leclerc, M. *Chem. Mater.* **1996**, *8*, 1512.
(15) Patil, A. O.; Ikonoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.
(16) Reynolds, J. R.; Sundaresan, N. S.; Pomerantz, M.; Basak, S.; Baker, C. K. *J. Electroanal. Chem.* **1988**, *250*, 355.
(17) Deb, S. K. *Appl. Opt. Suppl.* **1969**, *3*, 192.
(18) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, 1995.
(19) Granqvist, C. G.; Azens, A.; Isidorsson, J.; Kharrazi, M.; Kullman, L.; Lindstroem, T.; Niklasson, G. A.; Ribbing, C.-G.; Roennow, D.; Stromme Mattsson, M.; Veszelei, M. *J. Non-Cryst. Solids* **1997**, *218*, 273.
(20) Monk, P. M. S. *J. Electroanal. Chem.* **1997**, *432*, 175.
(21) Schwendeman, I.; Hickman, R.; Sonmez, G.; Schottland, P.; Zong, K.; Welsh, D. M.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3118.
(22) Bange, K. *Solar Energy Mater. Solar Cells* **1999**, *58*, 1.
(23) Granqvist, C. G.; Azens, A.; Hjelm, A.; Kullman, L.; Niklasson, G. A.; Ribbing, C.-G.; Roennow, D.; Stromme Mattsson, M.; Veszelei, M.; Vaivars, G. *Solar Energy* **1998**, *63*, 199.
(24) Agnihotry, S. A.; Pradeep; Sekhon, S. S. *Electrochim. Acta* **1999**, *44*, 3121.
(25) Rauh, R. D. *Electrochim. Acta* **1999**, *44*, 3165.
(26) Tracy, C. E.; Zhang, J.-G.; Benson, D. K.; Czanderna, A. W.; Deb, S. K. *Electrochim. Acta* **1999**, *44*, 3195.
(27) Pennisi, A.; Simone, F.; Barletta, G.; Di Marco, G.; Lanza, L. *Electrochim. Acta* **1999**, *44*, 3237.
(28) Meeker, D. L.; Mudigonda, D. S. K.; Osborn, J. M.; Loveday, D. C.; Ferraris, J. P. *Macromolecules* **1998,** *31*, 2943.
(29) Mudigonda, D. S. K.; Meeker, D. L.; Loveday, D. C.; Osborn, J. M.; Ferraris, J. P. *Polymer* **1999**, *40*, 3407.
(30) Brotherson, I. D.; Mudigonda, D. S. K.; Ocborn, J. M.; Belk, J.; Chen, J.; Loveday, D. C.; Boehme, J. L.; Ferraris, J. P.; Meeker, D. L. *Electrochim. Acta* **1999**, *44*, 2993.
(31) Byker, H. J. Gentex Corporation, US Patent No. 4902108.
(32) Mortimer, R. G. *Chem. Soc. Rev.* **1997**, *26*, 147.
(33) Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 1498.
(34) Sonmez, G.; Sonmez, H. B.; Shen, C. K. F.; Wudl, F. *Adv. Mater.* **2004**, *16*, 1905.
(35) Wyszecki, G.; Stiles, W. S. *Color Science, Art and Technology*; Elsevier: Amsterdam, 1998.
(36) Luo, Y.; Ruud, K.; Norman, P.; Jonsson, D.; Agren, H. *J. Phys. Chem. B* **1998**, *102*, 1710.
(37) Yurtsever, M.; Sonmez, G.; Sarac, A. S. *Synth. Met.* **2003**, *135−136*, 463.
(38) Sarac, A. S.; Sonmez, G. *Polym. Int.* **2002**, *51*, 594.
(39) Sonmez, G.; Schottland, P.; Zong, K.; Reynolds, J. R. *J. Mater. Chem.* **2001**, *11*, 289.

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