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Tailoring Electrochromic Properties through Discrete Electrochromes: Synthesis and Characterization of Poly[bis(5,2′-bithiophene-2-yl)dimethylsilane]

Dhurjati S. K. Mudigonda,[†] Jeffrey L. Boehme,[‡]
Ian D. Brotherston,[†] David L. Meeker,[§] and
John P. Ferraris*,[†]

*Department of Chemistry, Department of Physics,
The University of Texas at Dallas,
Richardson, Texas 75080, and US Engineer
Research and Development Center,
Vicksburg, Mississippi 39180*

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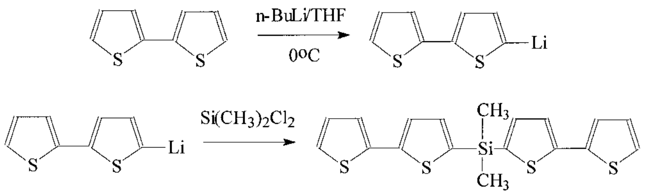
Conducting polymers have shown promise for use in such applications as ultracapacitors, light-emitting diodes, thin-film transistors, and electrochromic materials.[1] One novel application presently being considered is their use as active materials in military camouflage.[2,3] Polythiophenes in particular have been extensively studied for this purpose as their band gaps fall in the visible region of the electromagnetic spectrum. Linear polythiophenes generally exhibit a blue color upon oxidation despite various substitution patterns,[1] and the color in the doped state can be attributed to the delocalized electrochromes that lack well-defined structure. Although this color change may be important in some applications, for camouflage to be effective, it must contain those colors seen in nature, i.e., greens and browns. In contrast, nonconjugated polymers with pendant π-groups exhibit distinct color changes which can be attributed to their well-defined electrochromes.[4,5] In fact, earlier reports on the electrochromic properties of poly(vinylquaterthiophene) showed that this polymer, which contains discrete quaterthiophene units, exhibits a yellow-to-green color change from its neutral to oxidized state.[5] Unfortunately, the pendant groups in these nonconjugated polymers tend to irreversibly cross-link upon potential cycling ultimately altering the neutral color of the electrochromic material. Thus, although these polymers offer better control over the color, they lack long-term cyclability. Other studies directed at tailoring the electrochromic properties of polythiophenes have involved the use of various strategies including polymer blends and copolymers.[6] Another promising technique for obtaining the desired electrochromic behavior relies on synthetically defining the conjugation length of the electrochrome in the polymer backbone. This technique has been successfully used earlier to alter various electronic properties of polythiophenes such as photoluminescence and band gap.[7−9] Introduction of a silicon atom into the polythiophene backbone to limit the conjugation length, and the effects of potential dπ−pπ conjugation have been studied.[9,10] The advantages of using a silicon bridge extend beyond its ability to limit conjugation length. The electron-donating nature of the silicon atom also results in a lower oxidation potential that facilitates electropolymerization and may enhance the stability of the oxidized state. Furthermore, the silicon atom allows the attachment of various substituents without modifying the polymer's electronic structure. Similar effects can be achieved by introducing sp^3-C linkages in the backbone but routes to derivatize these positions with other substituents are tedious. We envisaged that such strategies might also lead to materials with better color control and improved electrochromic cyclability. In this communication, we report the synthesis and electrochromic properties of poly[bis(5,2′-bithiophene-2-yl)-dimethylsilane] **(PBTDMS)** which undergoes a reversible color change between its neutral (yellow) and oxidized (green) forms.

Scheme 1



The monomer **BTDMS** was synthesized in a two-step synthetic scheme (Scheme 1), involving lithiation of bithiophene at 0 °C followed by condensation with dichlorodimethylsilane. The typical yields were up to 65%. The compound was characterized by ^{1}H NMR and elemental analyses. The mass ratios found were satisfactory.[11]

Polymerization was achieved electrochemically from a solution containing 0.1 M of **BTDMS** and 0.2 M of $(CH_3)_4NCF_3SO_3$. The cyclic voltammogram of the resulting polymer on Pt was obtained by cycling in monomer-free electrolyte between 0 V and 0.9 V vs Ag/Ag$^+$ at 50 mV/s. The voltammogram, shown in Figure 1, depicts the characteristic p-doping/p-dedoping trace expected for conducting polymers based on thiophene repeat units. However, note that the onset of p-doping, ~0.25 V vs Ag/Ag$^+$ is lower than that of polythiophene due to the

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[†] Department of Chemistry, The University of Texas at Dallas.

[‡] Department of Physics, The University of Texas at Dallas.

[§] US Engineer Research and Development Center.

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(11) Experimental data: Mp 44−45 °C. ^{1}H NMR in ppm ($CDCl_3$): 7.3−6.9 (m, 10H, thienyl), 0.59 (s, 6H, $Si(CH_3)_2$). Calculated: C, 55.67%; H, 4.12%; S, 33%; Si, 7.22%. Found: C, 55.46%; H, 4.17%; S, 33.37%; Si, 7.88%.

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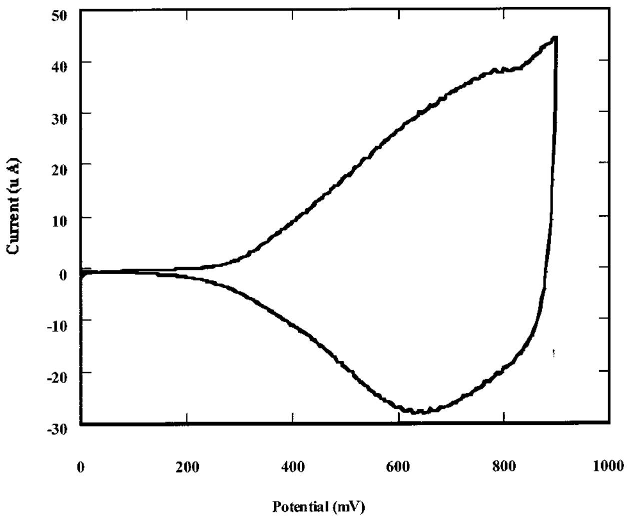

Figure 1. Cyclic voltammogram of **PBTDMS**.

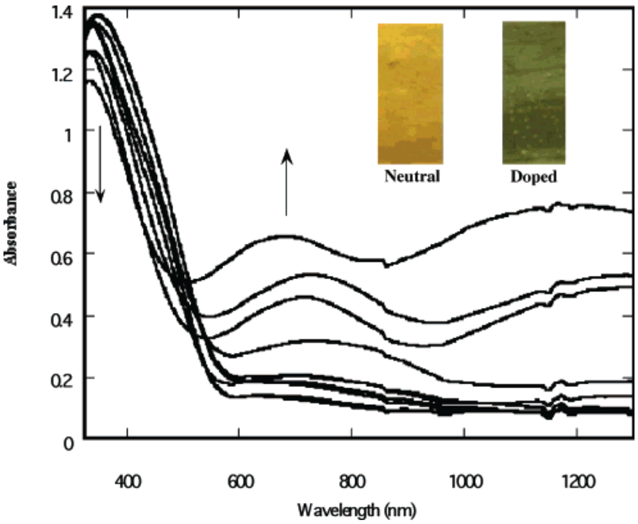

Figure 2. Variation in the absorption spectra of **PBTDMS** at 0 V and at 0.4–1.4 V with an increment of 0.2 V.

electron donating silyl groups in the polymer backbone. n-Doping was attempted on this polymer but none was observed.

The polymer was also grown onto an ITO/glass electrode used for in situ spectroelectrochemistry.[12] Figure 2 shows the absorption spectra obtained for **PBTDMS** at various applied potentials. Upon polymerization, the effective electrochrome consists of a quaterthiophene unit alternating with silylene units. The peak at 390 nm is attributed to the $\pi - \pi^*$ transition in this neutral electrochrome by analogy to the 391 nm transition observed for quaterthiophene.[13] Upon p-doping, a new peak is observed in the region 600–800 nm which grows with increasing potential. Further, this peak disappears upon dedoping the polymer. This absorption peak is comparable to the one observed for oxidized α,α′-dimethylquaterthiophene and thus can be attributed to the oxidized quaterthiophene unit in the polymer.[14]

The C–Si bond is reported to be stable to electrochemical cycling where the electrooxidation of tetra(terthienyl)silane was studied.[15] EDAX studies were carried out on the electropolymerized **BTDMS** to confirm this stability in our case. These experiments yielded a sulfur-to-silicon ratio of 4.19:1. Further support was obtained from elemental analyses. The calculated mass ratios for the polymer, **PBTDMS**, are C, 55.95%; H, 3.62%; S, 33.16%; and Si, 7.25%. The observed values are C, 53.83%; H, 2.73%; S, 33.4%; and Si, 9.88%. Mass percent of silicon was found by subtraction due to the insolubility of the polymer. If significant desilylation were occurring upon electrochemical cycling, it should lead to a material more closely resembling polythiophene. The calculated mass ratios for polythiophene are C, 58.5%; H, 2.43%; and S, 39.02%. Thus, desilylation would lead to an increase in the mass percentages of C and S which was not observed.

Electrochromic devices were fabricated with working electrodes consisting of an electrodeposited **PBTDMS** polymer film on an ITO/Mylar (Altair O) substrate. The counter electrode consisted of a spin-coated layer of vanadium pentoxide on ITO/Mylar. The supporting electrolyte was made by mixing 500 mg of poly(methyl methacrylate), 1.7 mL of propylene carbonate, 2 g of ethylene carbonate, and 100 mg of lithium tetrafluoroborate in 3 mL of acetonitrile. The observed color was quantitatively measured using a HunterLab Miniscan XE spectrocolorimeter and described in CIE 1976 $L^*a^*b^*$ coordinates. Detailed description of these measurements are described elsewhere.[2]

The neutral device appeared yellow to the naked eye corresponding to $L^* = 79.25$, $a^* = 1.34$, and $b^* = 36.2$. Upon oxidation (+2 V), the device appears green to the eye with $L^* = 76.42$, $a^* = -5.29$, and $b^* = 25.26$. This is to be contrasted with the electrochromic behavior of linear polythiophenes which appear in various colors in their neutral state and become blue in their oxidized state. Upon reduction (−2 V) the **PBTDMS** device returns to its yellow color. These devices could be cycled repeatedly between their yellow and green states.

In conclusion, an electrochromic polymer consisting of discrete electrochromes in the backbone has been synthesized and color control has been demonstrated. The observed color exhibited in the oxidized state of this polymer is relevant to dynamic camouflage applications. Further work is underway involving computational design and synthesis involving derivatizing both silylene and thienyl units for electrochromic materials with improved properties and desired color.

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(12) In situ spectroelectrochemistry was performed in a specially modified quartz cuvette described previously.[16] Spectra were recorded on a Perkin-Elmer Lambda 9 between 325 and 1300 nm with an incremental change to the applied potential.

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