High-Contrast Electrochromic Polymers from Alkyl-Derivatized Poly(3,4-ethylenedioxythiophenes)

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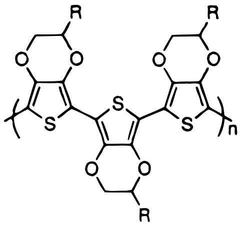
ABSTRACT: The syntheses of two new derivatives of 3,4-ethylenedioxythiophene (EDOT), specifically 5-octyldioxeno[2,3-*c*]thiophene (EDOT-C_8) (**2**) and 5-tetradecyldioxeno[2,3-*c*]thiophene (EDOT-C_{14}) (**3**), and their polymers are reported in this paper. Cyclic voltammetry of **2** and **3** in 0.1 M TBAP/CH_3CN show irreversible monomer oxidation peaks ($E_{\mathrm{p,m}}$) at 0.89 and 0.93 V, respectively. Multiple scans yield electroactive and conducting polymer films on electrode surfaces. The PEDOT-C_8 and PEDOT-C_{14} formed oxidize with relatively low peak potentials at −0.22 and −0.19 V, respectively, indicating the doped form of the polymer to be quite stable. Both PEDOT-C_8 and PEDOT-C_{14} show two reduction processes with peaks at −0.18 and −0.16 V ($E_{\mathrm{c2,p}}$) and −0.55 and −0.36 V ($E_{\mathrm{c1,p}}$) respectively. Optoelectrochemical studies reveal an E_g of 1.75 eV for both polymers. The polymers are electrochromic, relatively transmissive and light gray in the oxidized form, while being opaque and deep purple in the reduced form exhibiting high electrochromic contrasts. Long term switching studies carried out in 0.1 M $LiClO_4$/PC with Li/Li^+ as a reversible counter electrode shows that PEDOT, PEDOT-C_8, and PEDOT-C_{14} retained 65%, 50%, and 62% of their electroactivity after 6000, 9000, and 16 000 double switches, respectively.

Introduction

The synthesis of electroactive and conducting polymers having low oxidation potentials yields materials of high ambient stability in the conducting state. Of the many conducting polymers now studied, polypyrrole[2] and polyaniline[3] stand out for their ease of oxidation and stability making them the materials of choice to date for applications and commercial consideration. Among other conjugated heterocyclic polymers that have been studied extensively, polythiophenes have attracted attention due to their ease of derivatization and ability to be polymerized by a variety of chemical and electrochemical methods.[4,5] While unsubstituted polythiophenes are insoluble and infusible, alkyl chain derivatization at the 3-position induces solubility and fusibility, making them true thermoplastics.[6] At the same time, the elevated oxidation potentials of the poly(3-alkylthiophenes), relative to polypyrrole and polyaniline, cause their oxidized and conducting forms to be less stable. The incorporation of electron-donating substituents onto a conjugated chain is a commonly employed strategy to decrease the polymer's oxidation potential by raising the energy of the valence band electrons ("HOMO" of the conjugated chain). At the same time, there is a smaller perturbation on the energy of the conduction band ("LUMO" of the conjugated chain), which leads to a decrease in the polymer's electronic band gap.[7] This band gap reduction was also effected in the case of poly(isothianaphthene) by fusing a benzenoid ring to the 3 and 4 positions of thiophene yielding highly transmissive films in the doped and highly conducting state.[8] In general, disubstitution at the 3 and 4 positions, which eliminates the possibility of β coupling and reduces the likelihood of cross-linking, leads to severe steric interactions and reduces the extent of conjugation. This is overcome by fusing the ring onto the heterocycle, effectively pinning the substituents back from the main chain.

Poly(ethylenedioxythiophene) (PEDOT, **1**, R = H), with dioxane rings fused to the *c* face of thiophene, also presents less steric demands than those encountered with a disubstituted polythiophene. In addition, PEDOT has a lower oxidation potential than other polythiophenes reported and is quite stable under ambient and elevated temperature conditions.[9] This polymer has been shown to be useful as an antistatic material[10] and as a solid electrolyte in capacitors.[11] Thin films of the unsubstituted polymer are a transmissive blue-gray in their oxidized state, and a highly absorbing blue-violet in their reduced state, suggesting its use as a cathodically coloring electrochromic material.[12]



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Within our investigations delineating main chain structure and substituent effects on the properties of electrochromic polymers,[13] we have synthesized the octyl- and tetradecyl-substituted poly(ethylenedioxythiophenes) (PEDOT-C_8, **1**, R = C_8H_{17}, and PEDOT-C_{14}, **1**, R = $C_{14}H_{29}$) derivatives. We find these materials to provide excellent cathodically coloring electrochromic properties of high optical contrast throughout the visible region, along with a high degree of redox stability. In addition, we have prepared soluble versions of these polymers which can be solution processed to form electrochromic films.[13e] This paper outlines the structure−property relationships in these polymers and compares them to the parent PEDOT and the recently reported PEDOT-C_6 and similar derivatives.[14]

Results and Discussion

Monomer Synthesis. The EDOT monomers were synthesized by modifying methods first reported by Fager and developed further by others.[15] After preparation of the reported disodium salt of 2,5-dicarbethoxythiophene 3,4-dioxide and acidification to the diol, ring

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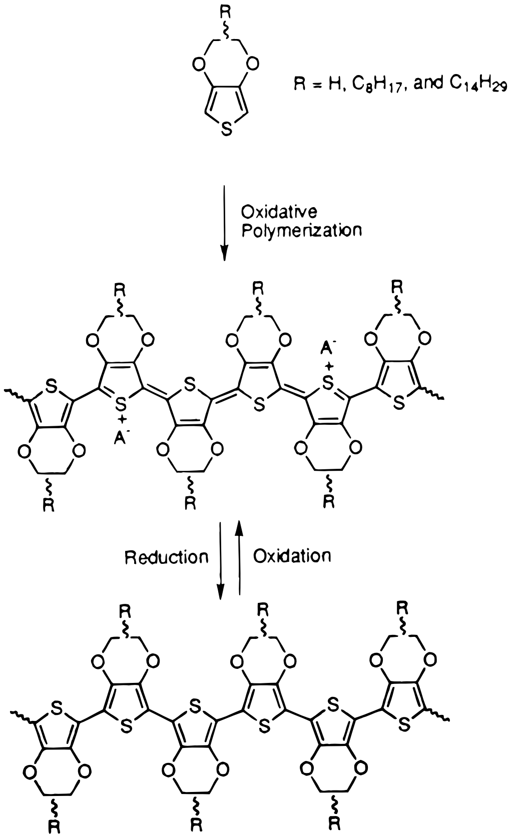
Scheme 1



closure was effected by reaction with the appropriate 1,2-dibromoalkane (prepared from bromine and the required alkene) in anhydrous DMF to yield the alkyl-substituted (octyl and tetradecyl) 2,5-dicarboethoxy-3,4-ethylenedioxythiophenes. Hydrolysis of the diester thiophene to the diacid was followed by decarboxylation in quinoline with copper chromite to yield the monomers 5-octyldioxeno[2,3-*c*]thiophene (**2**, EDOT-C_8) and 5-tetradecyldioxeno[2,3-*c*]thiophene (**3**, EDOT-C_{14}).

Electrochemical Polymerization. EDOT, EDOT-C_8 (**2**), and EDOT-C_{14} (**3**) were electrochemically polymerized to yield electrode-supported electroactive polymer films using a number of solvent/electrolyte combinations as illustrated by the general electropolymerization path outlined in Scheme 1. The parent monomer, EDOT, exhibits a monomer oxidation peak ($E_{\mathrm{p,m}}$) at 1.0 V while EDOT-C_8 and EDOT-C_{14} exhibit $E_{\mathrm{p,m}}$ values at 0.89 and 0.92 V, respectively, in 0.1 M TBAP/CH_3CN. During an initial anodic scan, the monomers are oxidized to form cation radicals as illustrated in Figure 1 for PEDOT-C_{14}. These cation radicals subsequently polymerize and deposit as electroactive polymer films on the working electrode surface. On the cathodic scans of the cyclic voltammograms (CVs) of the polymers, two reduction processes are evident. PEDOT-C_8 reduces with peaks at -0.18 V ($E_{\mathrm{c2,p}}$) and -0.55 V ($E_{\mathrm{c1,p}}$), while EDOT-C_{14} reduces with peaks at -0.16 V ($E_{\mathrm{c2,p}}$) and -0.36 V ($E_{\mathrm{c1,p}}$), attributable to reduction of the oxidized polymer that has formed on the electrode surface. These multiple reductions have been observed for other conducting polymers and may be due to sequential reduction of dicationic bipolaronic charge carriers initially to cation radical polaronic charge carriers and then to neutral polymer or may be due to the ion transport properties of the polymer.[16] The PEDOT-C_8 formed reoxidizes at -0.22 V ($E_{\mathrm{a,p}}$), while the PEDOT-C_{14} formed re-oxidizes at -0.19 V ($E_{\mathrm{a,p}}$). As the electropolymerization of these monomers is continued by repeated scanning, the oxidation and reduction peak currents increase and shift slightly in potential. This increased current is due to buildup of the electroactive polymer on the electrode surface. Analysis of the CV behavior of the polymers in monomer-free electrolyte shows all of the peak currents to scale linearly with scan rate, indicating that the polymer (and thus all electroactive sites) is well-adhered to the surface of the electrode.

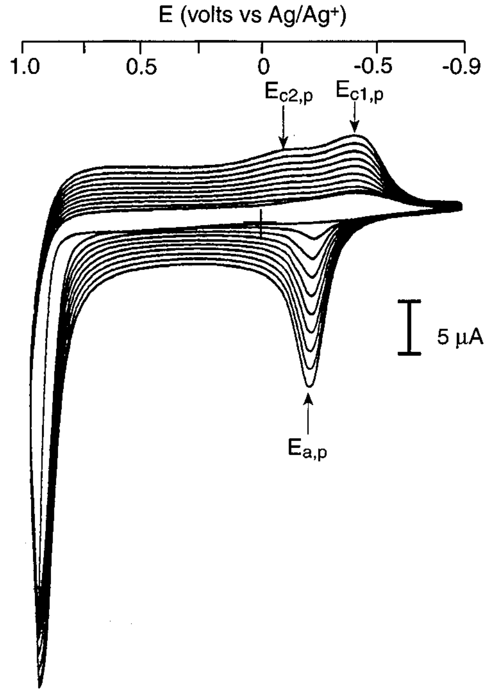


Figure 1. Repeated potential scan electropolymerization of EDOT-C_{14} at 100 mV/s in 0.1 M TBAP/CH_3CN.

Solvent and Electrolyte Dependence of Electropolymerization. EDOT-C_8 and EDOT-C_{14} were polymerized by the repeated scanning methodology onto ITO-coated glass in a series of solvent/electrolyte systems and their electrochemical properties during film growth compared as shown in Table 1. Both PEDOT-C_8 and PEDOT-C_{14} show two reductive processes in 0.1 M $LiClO_4$/CH_3CN and 0.1 M TBAP/CH_3CN while in 0.1 M $LiClO_4$/PC and 0.1 M TBAP/CH_2Cl_2 only one broad reduction was observed. A fifth electrolyte system, 0.1 M $LiClO_4$/tetraglyme, was attempted as an electropolymerization medium but did not allow for the deposition of electroactive polymer. It is likely that the charged oligomers forming at the electrode surface were solublized by the tetraglyme medium, preventing deposition and film formation.

Examination of the results in Figure 1 and Table 1 shows the monomer to effectively electropolymerize between 0.8 and 1.0 V. This electropolymerization potential is significantly lower than that observed for 3-methylthiophene polymerization (+1.5 V) and close to that for pyrrole polymerization. This relatively low polymerization potential for a single heterocyclic ring monomer is important as side reactions that occur at high potential are avoided and the electropolymerization proceeds efficiently. The polymer redox processes occur at potentials slightly below 0.0 V indicating that formation of the doped forms of the polymers is facile and they are quite stable, comparable to the parent PEDOT.

The electropolymerization efficiency was studied in more detail by comparing the amount of electroactive

Table 1. Electrochemical Potentials[a] for Monomer Oxidation and Polymer Redox Electroactivity

polymerization electrolyte system	EDOT-C_8				EDOT-C_{14}			
	$E_{p,m}$	$E_{a,p}$	$E_{c2,p}$	$E_{c1,p}$	$E_{p,m}$	$E_{a,p}$	$E_{c2,p}$	$E_{c1,p}$
0.1 M TBAP/CH_3CN	0.89	−0.22	−0.14	−0.52	0.92	−0.19	−0.14	−0.32
0.1 M TBAP/CH_2Cl_2	0.96	−0.24	− 0.56		0.96	−0.22	− 0.54	
0.1 M $LiClO_4$/PC	1.01	0.05	− 0.3		0.78	−0.15	− 0.2	
0.1 M $LiClO_4$/tetraglyme	no polymer was deposited on the electrode surface, as the oligomers dissolved							
0.1 M $LiClO_4$/CH_3CN	1.0	−0.2	−0.2	−0.5	0.96	−0.1	−0.2	−0.44

[a] Volts versus Ag/Ag^+ (0.01 M) reference electrode.

Table 2. Solvent/Electrolyte Dependence of Polymer Redox Electroactivity

redox switching electrolyte system	peak anodic current response (μA)[a]		
	PEDOT	PEDOT-C_8	PEDOT-C_{14}
0.1 M $LiClO_4$/CH_3CN	235	162	64
0.1 M TBAP/CH_3CN	115	84.6	33.8
0.1 M $LiClO_4$/PC	46	42	22
0.1 M TBAP/CH_2Cl_2	38	20	14.4

[a] Cyclic voltammograms run at 100 mV/s on polymer films deposited during 10 cyclic scans between −0.8 and 1.0 V in 10 mM of monomer solution of the same solvent/electrolyte combination.

polymer deposited with a set number of repeated scans as a function of electrodeposition medium. The anodic current response for the polymer oxidation on the tenth scan during deposition was monitored and is shown in Table 2. It can be seen that the electrodeposition rate of EDOT proceeds more rapidly than that for EDOT-C_8, which is more rapid than EDOT-C_{14} in all of the solvent/electrolyte systems studied. This can be attributed to solubilization of the oligomers forming at the electrode surface by the long alkyl chains. Comparing solvents, it can be seen that the deposition is most efficient in CH_3CN-based electrolytes and least efficient in CH_2Cl_2. This is as expected as CH_2Cl_2 is generally a good solvent for alkyl-derivatized thiophene polymers. In a practical sense, 0.1 M $LiClO_4$/CH_3CN was found to serve as the best electrodeposition medium for the EDOT and alkyl-substituted EDOT polymers studied here.

Optoelectrochemical Analyses. In order to probe the electronic structure of the polymers, and to examine the optical changes that occur during redox switching which are important for electrochromic applications, optoelectrochemical analyses were carried out. Recent work by Havinga et al. studying the optoelectrochemical response of PEDOT-C_6 is consistent with our results.[14] Films were potentiostatically synthesized from 10 mM monomer and 0.1 M $LiClO_4$/CH_3CN solution on an ITO-coated glass electrode at 1.1 V. After the film was rinsed with monomer-free electrolyte, the polymer-coated ITO glass electrode was used as the working electrode, along with Ag/Ag^+ (0.01 M) as reference and platinum as counter electrodes in 0.1 M $LiClO_4$/CH_3CN. The optoelectrochemical spectral series was monitored while scanning from 300 nm (4.1 eV) to 1600 nm (0.78 eV) as the polymer was sequentially stepped between its fully oxidized and fully reduced forms. Neutral PEDOT exhibits an electronic band gap (E_g), defined as the onset for the π to π^*absorbance, of approximately 1.7 eV and has a strong peak at 2.2 eV causing the films to be deep blue and absorbing. As the potential is sequentially increased, this peak reduces in intensity, with the concomitant growth of a low-energy absorption at 1.4 eV. In the highly oxidized state a continuous absorption band through the near-IR is observed which tails into the visible region of the spectrum, leaving the film in a sky blue and relatively transmissive state.

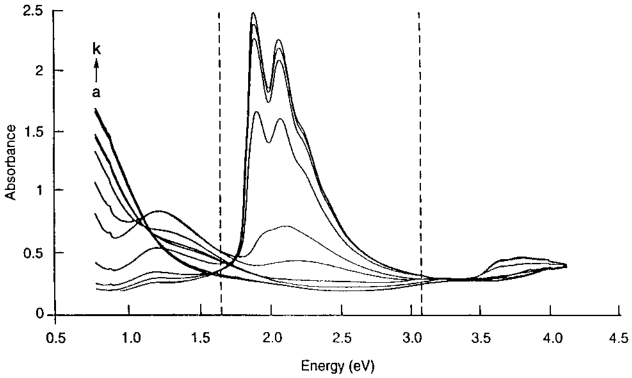


Figure 2. Optoelectrochemical spectra for PEDOT-C_{14} as a function of applied potential between −0.8 and +0.8 V in 0.1 M TBAP/CH_3CN: (a) −0.8 V, (b) −0.6 V, (c) −0.4 V, (d) −0.3 V, (e) −0.2 V, (f) −0.1 V, (g) 0.0 V, (h) +0.2 V, (i) +0.4 V, (j) +0.6 V, (k) +0.8 V.

Figure 2 shows the optoelectrochemical series for a PEDOT-C_{14} film synthesized using the methodology described for PEDOT at a constant potential of 1.0 V. The absorbance was monitored *in situ* as a function of potential between −0.8 and 1.0 V. In the reduced, neutral, form the polymer exhibits a high absorbance throughout the visible region (1.7−3.1 eV denoted between the dashed lines) and is a deep purple in color. As the potential is increased, the visible absorbance decreases to the point that the film is light gray and highly transmissive when oxidized. Similar behavior is found for PEDOT-C_8. The E_g values of both PEDOT-C_8 and PEDOT-C_{14} are approximately 1.75 eV.

Comparisons of the optoelectrochemical spectra for PEDOT and the alkyl-substituted PEDOTs bring out important similarities and differences in the substituted and nonsubstituted polymers. In the neutral state, PEDOT exhibits a single broad absorption, while the interband transition for PEDOT-C_{14} (along with PEDOT-C_8) is split into two distinct peaks at 1.9 and 2.1 eV and an accompanying high-energy shoulder at 2.2 eV. This splitting can be attributed to vibronic coupling and suggests a relatively high degree of regularity along the polymer chain.[17] With oxidative doping, both PEDOT and PEDOT-C_{14} lose absorption throughout the visible region due to depletion of the interband transition, while concurrently increasing absorption in the near-IR region due to formation of bipolaronic bands. PEDOT exhibits an increase of its near-IR absorption with a peak evolving at 1.4 eV along with a low-energy absorbance below 1 eV. In the case of PEDOT-C_{14} shown in Figure 2, a peak evolves at 1.25 eV. Above an applied potential of 0.0 V the peak at 1.25 eV decreases significantly in intensity as absorption continues to increase at 0.8 eV. At the highest oxidation levels, the interband transition and the transistion at 1.25 eV are completely eliminated, while the absorbance

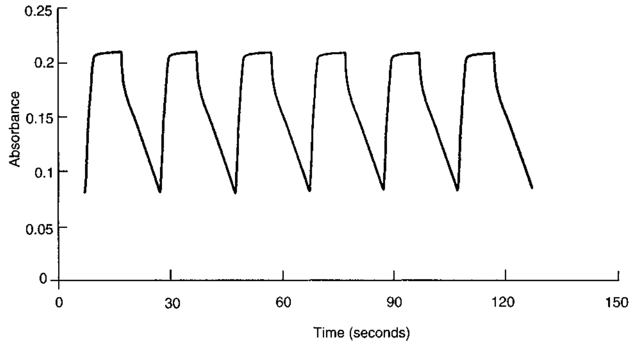


Figure 3. Electrochromic switching, optical absorbance change monitored at 600 nm for the 135th to 140th switch of PEDOT at 600 nm in 0.1 M TBAP/CH_3CN.

at 0.8 eV reaches a maximum. This causes the PEDOT-C_{14} to have significantly less absorption throughout the visible region when compared to unsubstituted PEDOT. With this, the electrochromic contrast in the visible region is greater for the substituted polymers, making them better candidates for electrochromic devices. At high potentials the bipolaronic bands coalesce with the valence and conduction bands giving rise to only a single absorption at low energy.[18]

The optoelectrochemical spectral series for PEDOT-C_{14} was examined using two further electrolyte/solvent systems for growth and switching (0.1 M $LiClO_4$/PC and 0.1 M TBAP/CH_3CN). In both cases, essentially identical band gaps, transition energies, existence, and energies of isosbestic points were found. The major difference was the relative absorbance values, though each film was deposited with an identical amount of charge passed during electropolymerization. The absorbance at λ_{max} (*ca.* 1.9–2.0 eV) for the neutral polymer was found to 2.4, 1.7, and 0.8 for films synthesized and switched in $LiClO_4$/CH_3CN, TBAP/CH_3CN, and $LiClO_4$/PC, respectively. This scales with the polymer's anodic current response results reported in Table 2 and serves as a confirmation of the solvent/electrolyte dependence for the efficiency of electropolymerization.

Electrochromic Switching Studies. Electrochromic switching studies were carried out to monitor absorbance changes with time during repeated potential stepping between reduced and oxidized states to obtain an insight into changes in the optical contrast. In an initial experiment illustrated in Figure 3, the parent PEDOT was switched by stepping the potential between −1.1 and +1.1 V with a switching interval of 10 s in a 0.1 M TBAP/CH_3CN electrolyte while monitoring the absorbance at 600 nm. The polymer film repeatedly and reproducibly changed from a dark blue absorptive reduced state at −1.1 V to a light gray transmissive oxidized state at +1.1 V with a high contrast. By examination of one of the double potential switches in Figure 4, it can be seen that the reductive process proceeds significantly more rapidly than the oxidation process. While the reduction is complete in *ca.* 2.5 s, reoxidation requires greater than 10 s. The rapidity of the reduction can be attributed to the ease of transport through the conducting film to the electrode contact. Reoxidation of the neutral film initiates at the insulating polymer–electrode interface, and a conducting front propagates through the film's thickness. Within the time scale of this experiment, the change in optical absorption had not leveled off, making quantitation of film transmittance difficult.

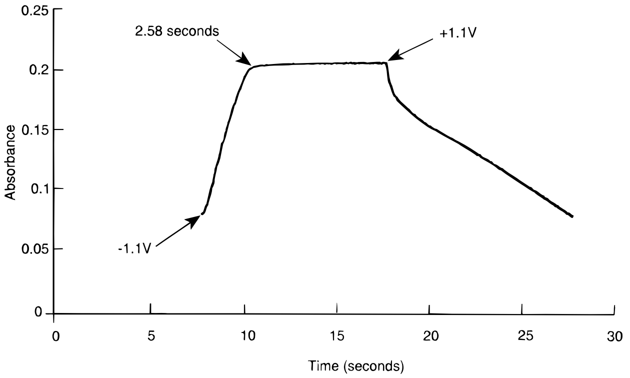


Figure 4. Electrochromic switching, optical absorbance change monitored at 600 nm for the 38th switch of PEDOT in 0.1 M TBAP/CH_3CN.

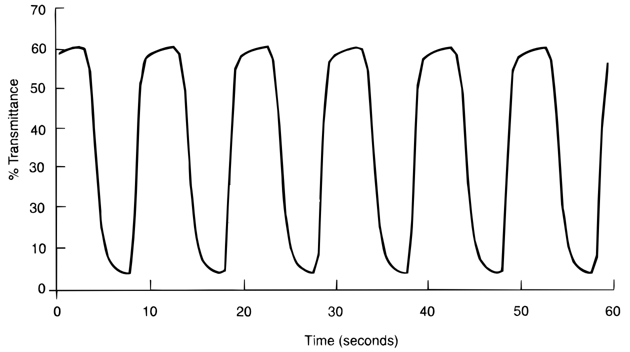


Figure 5. Electrochromic switching, optical absorbance change monitored at 600 nm for the 16th to 21st switch of PEDOT-C_{14} in 0.1 M TBAP/CH_3CN.

We find the alkyl-substituted polymers to be significantly faster in their redox switching rates, while at the same time exhibiting a higher degree of electrochromic contrast, when compared to the unsubstituted PEDOT. For example, Figure 5 shows the switching of PEDOT-C_{14} between −0.8 and +0.6 V with a switching interval of 5 s in 0.1 M TBAP/CH_3CN. In this instance, both the fully oxidized and fully reduced states are reached as evidenced by the leveling off of the optical response. The optical contrast is quite high for PEDOT-C_{14}, consistent with the optoelectrochemical results discussed earlier, as the oxidized film was 60% transmissive while the reduced film was less than 5% transmissive. After 1800 double potential switches in this electrolyte, the optical contrast exhibited a slight decrease to 55% transmission in its oxidized form and 10% transmission in its reduced form.

Upon changing the electropolymerization and redox switching the medium to 0.1 M $LiClO_4$/CH_3CN, both PEDOT-C_8 and PEDOT-C_{14} were found to switch significantly more rapidly. This is illustrated by the single switch in Figure 6, which shows PEDOT-C_8 to fully reduce in less than 0.1 s and reoxidize in 1–2 s. In this instance, the optical absorbance changes clearly level off with each switch demonstrating the importance of ion transport characteristics on switching rates. In these optoelectrochemical experiments, the alkyl-derivatized polymers were found to be more durable than the unsubstituted polymer when exposed to multiple switches. For example, PEDOT-C_{14} retained more than 70% of its electroactivity after 1100 switches, while the parent PEDOT retained less than 50% of its electroactivity after 140 switches.

In the optoelectrochemical experiments, a platinum plate (modified for use in the spectrophotometer) was used as a counter electrode while the films were

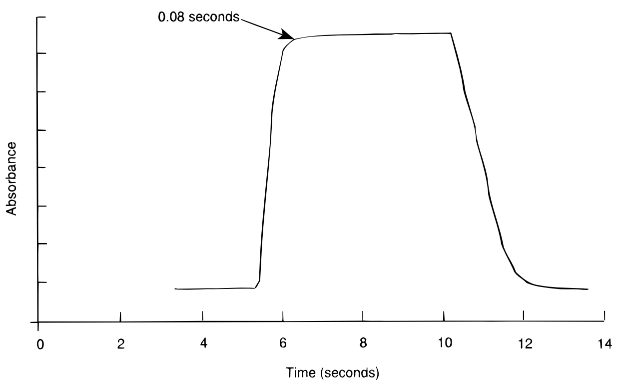


Figure 6. Electrochromic switching optical absorbance change monitored at 600 nm for the 335th switch of PEDOT-C_8 in 0.1 M $LiClO_4/CH_3CN$.

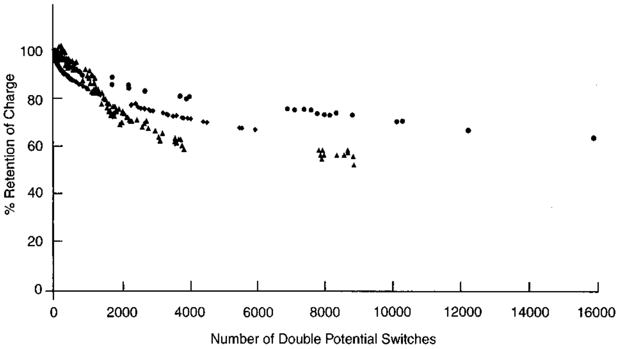


Figure 7. Long term switching charge retention as a function of the number of double potential switches (switching interval = 5 s) for PEDOT (◆), PEDOT-C_8 (▲), and PEDOT-C_{14} (●) utilizing $Li^0/LiClO_4$, propylene carbonate/polymer redox couple.

deposited on transparent ITO working electrodes. As such, the redox processes occurring at the Pt counter were ill-defined and could be contributing detrimental side products which may react with the electroactive polymer. The result would be polymer degradation which decreases the life of the electrochemical cell.

To more accurately determine the stability of these polymers to multiple redox switches, a well-defined electrochemical reaction at the counter electrode was chosen. In this instance, we employed Li metal in a 0.1 M $LiClO_4$/PC based electrolyte under a carefully dried argon atmosphere. Polymer films were potentiostatically synthesized on ITO-coated glass electrodes at +1.1 V under an argon blanket. Lithium counter electrodes were prepared in an argon atmosphere drybox. Lithium metal was flattened into a thin sheet, contacted to platinum wire, and placed into a glass jacket open on both the ends. Only the lithium end of the electrode was allowed to contact electrolyte during the long term switching experiments.

PEDOT was switched by stepping the potential between −1.1 and +1.1 V with a switching interval of 10 s. PEDOT-C_8 and PEDOT-C_{14} were switched between −0.8 and 0.6 V with a switching interval of 5 s. The change in charge per potential step was monitored relative to the initial charge as a function of the number of double potential switches as shown in Figure 7. Under these conditions, all three polymers showed a high retention of electroactivity. At the same time, visual observation of the electrochromic process indicated the films to retain a high degree of electrochromic contrast. In these experiments, PEDOT-C_8 was switched over 9000 times with a retention of 50% of its electroactivity while PEDOT retained 65% of its electroactivity after 6000 double potential switches. PEDOT-C_{14} retained over 60% of its electroactivity even after 16 000 double potential switches. It should be noted that these long term switching studies are meant to be diagnostic only of the long lifetimes possible with EDOT-based electrochromic polymers. Actual device lifetimes are based on many variables (materials, construction methods, impurity levels, operating conditions, etc.) and practical device lifetimes may greatly exceed those measured here.

Experimental Section

Thiodiglycollic acid, diethyl oxalate, DMF (anhydrous), bromine, dodecene, hexadecene, KOH, and copper chromite were used as purchased from Aldrich Chemical. Absolute ethanol was obtained from Aaper Alcohol and Chemical Co. and used as received. K_2CO_3 was dried under vacuum overnight at 110 °C. Quinoline was dried in Na_2SO_4 and vacuum distilled over zinc dust. CH_3CN was freshly distilled over CaH_2. TBAP was recrystallized from ethyl acetate. $LiClO_4$ was recrystallized from CH_3CN, melted under vacuum at 110 °C, and subsequently allowed to cool under vacuum. Propylene carbonate was exposed to 4-Å molecular sieves for 2 days, before vacuum distillation. Distilled propylene carbonate was stored over molecular sieves and under an argon atmosphere.

^1H- and ^{13}C-NMR spectroscopies were carried out on Varian Gemini-300 and Varian XL-300 spectrometers. Infrared spectroscopy was carried out on a Biorad FTS-40 FTIR. Mass spectrometry was carried out on a Finnigan MAT 95Q mass spectrometer. Elemental analysis was accomplished at Atlantic Microlab, Inc., and Robertson Microlit Laboratories, Inc.

Cyclic voltammetry was conducted utilizing platinum button working, platinum plate counter, and Ag/Ag^+ reference electrodes. Potentials were controlled using an EG&G PAR Model 273 potentiostat/galvanostat. Optoelectrochemical spectroscopy was carried out on a Varian Cary 5E UV-Vis-NIR spectrophotometer. Polymer films for optoelectrochemical measurements were prepared potentiostatically (between 35 and 40 mC/cm^2) on ITO-coated glass slides (Delta Technologies) as the working electrode. PEDOT was synthesized at 1.2 V while both PEDOT-C_8 and PEDOT-C_{14} were synthesized at 1.1 V. Platinum plates and 0.01 M Ag/Ag^+ were used as the counter and reference electrodes, respectively. During electrochemical experiments, all electrolytes were purged with argon prior to use and an argon blanket retained over the cell. The polymer films were washed with monomer-free electrolyte before use in either optoelectrochemistry or long term switching studies.

Diethyl Thioglycollate.[15] Thiodiglycollic acid (300 g) was refluxed with 1000 mL of absolute ethanol in a 2 L one-necked round-bottomed flask fitted with a condenser and drying tube in the presence of 2 mL of H_2SO_4 as a catalyst. After the reaction mixture was refluxed for 12 h, 700 mL of ethanol and water was azeotropically distilled off. Absolute ethanol (500 mL) was added and refluxed for 20 h. The mixture was washed with water to remove ethanol and acid and subsequently extracted with ether. The ether layers were combined, dried with anhydrous $CaCl_2$, and concentrated. Vacuum distillation yielded a colorless liquid with a strong sulfurous odor. Yield = 337 g (91%).

Disodium Salt of 2,5-Dicarbethoxythiophene 3,4-Dioxide.[15] Sodium ethoxide was freshly prepared by dissolving, in portions, 32.7 g of Na in 1500 mL of absolute ethanol in a 3 L flask fitted with a mechanical stirrer and a 250 mL dropping funnel under a blanket of argon. Slowly a mixture of 115 g (0.558 mol) of diethyl thioglycollate and 83.5 g (0.571 mol) of oxalyl chloride in 50 mL of absolute ethanol was added into the reaction vessel dropwise overnight with constant stirring. A thick curdy yellow precipitate of the disodium salt formed immediately. The mixture was warmed for 2 h to 50 °C to complete the reaction. The solution was vacuum filtered and the precipitate washed with ethanol and subsequently air-dried to quantitatively yield a finely powdered bright yellow product.

2,5-Dicarbethoxy-3,4-dihydroxythiophene.[15] The disodium salt of 2,5-dicarbethoxythiophene 3,4-dioxide (100 g, 0.36 mol) was dissolved in 1500 mL of distilled water and 300 mL of 1 M HCl was added slowly dropwise with constant stirring until the solution became acidic. Immediately, thick white precipitate fell out. After filtration, the precipitate was washed with water and air-dried. Recrystallization from ethyl acetate yielded white shiny crystals. Mp 130−132 °C. ^{1}H-NMR (d, ppm, TMS reference): 1.35 (t), 4.35 (q), 9.36 (s). ^{13}C-NMR: 14, 62.0, 107, 152, 166. Yield = 72.5 g (86%).

2,5-Dicarbethoxy-3,4-ethylenedioxythiophene.[15] 2,5-Dicarbethoxy-3,4-dihydroxythiophene (0.980 g, 3.85 mmol) was refluxed at 90 °C with 1,2-dibromoethane (0.715 g, 3.85 mmol) and anhydrous K_2CO_3 (0.951 g, 9.62 mmol) in anhydrous DMF (10 mL) for 24 h. This resulted in formation of a burgundy viscous liquid with some yellow solids at the bottom of the flask. The mixture was cooled to room temperature, poured into 50 mL of hot acetone, stirred for 10 min, and filtered. Fifty milliliters of pentane was added and the mixture washed repeatedly with water to remove DMF, dried, and concentrated. Recrystallization from ethyl acetate yielded a white solid. Yield = 0.76 g (70%). ^{1}H-NMR (δ, ppm, TMS reference): 1.35 (t), 4.35 (q), 4.4 (s). ^{13}C-NMR: 16, 61.0, 62.5, 112.0, 145.0, 161. MS: molecular ion peak, 287 amu.

2,5-Dicarboxy-3,4-ethylenedioxythiophene.[15] 2,5-Dicarbethoxy-3,4-ethylenedioxythiophene (0.5 g, 1.7 mmol) was added to an excess 5% NaOH aqueous solution and refluxed. The solid slowly dissolved after refluxing for 6 h. The solution was cooled and slowly acidified with concentrated H_2SO_4 until the solution became highly acidic, which caused a slow precipitation. The solution was cooled in the freezer to complete precipitation and the product was filtered, washed well with water, and oven-dried to yield a white solid. Yield = 0.29 g (74%). ^{1}H-NMR (δ, ppm, TMS reference): 4.3 (s), 13.2 (b). ^{13}C-NMR: 62.5, 112.0, 143.5, 162.0. MS: molecular ion peak, 231 amu.

3,4-Ethylenedioxythiophene.[15] 2,5-Dicarboxy-3,4-ethylenedioxythiophene (1 g, 4.3 mmol) was refluxed in quinoline with 4% copper chromite as a catalyst at 160 °C for 6 h under argon. After cooling to room temperature, the reaction mixture was added into 25 mL of pentane, stirred, and filtered through Celite. The filtrate was washed repeatedly with water and 1 M HCl. The organic layer was dried with anhydrous $CaCl_2$, and flash chromatography yielded a colorless liquid. Yield = 0.63 g (48%). ^{1}H-NMR (δ, ppm, TMS reference): 4.2 (s), 6.32 (s). ^{13}C-NMR: 65, 110, 142. (Note: 3,4-ethylenedioxythiophene has recently been made commercially available by Bayer AG.)

2,5-Dicarbethoxy-5-octyldioxeno[2,3-*c*]thiophene. Ten grams (0.0385 mol) of 2,5-dicarbethoxy-3,4-dihydroxythiophene was dissolved in 80 mL of anhydrous DMF in a 250 mL 3NRBF under argon. Twelve grams (0.0868 mol) of K_2CO_3 and 13 g (0.0435 mol) of 1,2-dibromodecane (prepared from 1-decene and bromine) were introduced, and the mixture was heated to 110 °C for 48 h. After cooling, the reaction mixture was stirred with 100 mL of diethyl ether and the dark brown liquid filtered. The filtrate was washed with deionized water, and the aqueous layer was extracted with ether. The organic solutions were combined, dried with anhydrous $CaCl_2$, and concentrated to yield a whitish brown solid. Recrystallization from ether yieled a white, powdery solid. Yield = 15.1 g (52.2%). Mp 92−94 °C. Anal. Calcd: C, 60.32; H, 7.53; S, 8.03; O, 28.04. Found: C, 60.25; H, 7.46; S, 8.02; O, 27.67. ^{1}H-NMR (δ, ppm, TMS reference): 0.71−0.99, 1.09−1.92, 3.92−4.13, 4.17−4.55. ^{13}C-NMR: 14.0, 14.04, 22.65, 24.99, 29.21, 29.40, 29.46, 30.66, 31.83, 61.5, 68.47, 112, 112.5, 141.72, 142.21, 161. MS: molecular ion, 398.19 amu; base peak, 213.99 amu.

5-Octyldioxeno[2,3-*c*]thiophene-2,5-dicarboxylic Acid. The diester 2,5-dicarbethoxy-5-octyldioxeno[2,3-*c*]thiophene (0.7 g, 1.76 mmol) was hydrolyzed by refluxing in 30 mL of 10% KOH for 8 h to completely dissolve the ester. After cooling to room temperature the reaction mixture was added dropwise into 100 mL of 0.1 M HCl. The milky white precipitate was collected by vacuum filtration, washed with copious amount of water, and dried. Yield = 0.62 g (74%). Mp 216−220 °C. Anal. Calcd: C, 56.13; H, 6.5; S, 9.36. Found: C, 55.92; H, 6.43; S, 9.66. ^{1}H-NMR (δ, ppm, TMS reference): 0.75−0.96, 1.11−1.75, 3.93−4.13, 4.20−4.53, 13.1. ^{13}C-NMR: 13.97, 22.13, 24.29, 28.65, 28.81, 28.89, 29.65, 31.31, 67.46, 73.70, 111.42, 111.53, 144.61, 144.87, 161.79. MS: molecular ion peak, 342.11 amu; base peak, 55.07 amu.

2,5-Dicarbethoxy-5-tetradecyldioxeno[2,3-*c*]thiophene. 2,5-Dicarbethoxy-3,4-dihydroxythiophene (8.3 g, 0.0385 mol) was dissolved in 80 mL of anhydrous DMF in a 250 mL 3NRBF under argon. Eleven grams (0.0798 mol) of K_2CO_3 and 13.5 g (0.035 mol) of 1,2-dibromohexadecane (prepared from 1-hexadecene and bromine) were introduced, and the mixture was heated to 90 °C for 48 h. After cooling to room temperature, the reaction mixture was stirred with 100 mL of hot diethyl ether and the dark brown liquid filtered. The filtrate was washed with deionized water, and the aqueous layer was extracted with ether. The organic solutions were combined, dried with anhydrous $CaCl_2$, and concentrated to yield a whitish brown solid. Recrystallization from a 4:1 ether/methanol mixture yielded a whitish particulate solid. Yield = 4.5 g (24%). Mp 70−74 °C. Anal. Calcd: C, 64.77; H, 8.77; S, 6.63. Found: C, 65.27; H, 9.06; S, 6.53. ^{1}H-NMR (δ, ppm, TMS reference): 0.85−0.92, 1.2−1.85, 3.9−4.8. ^{13}C-NMR: 14.08, 14.26, 22.69, 24.92, 29.35, 29.41, 29.53, 29.65, 30.41, 31.93, 61.14, 61.22, 68.40, 74.25, 1287.51, 145.02, 160.90. MS: molecular ion peak, 482 amu; base peak, 55 amu.

5-Tetradecyldioxeno[2,3-*c*]thiophene-2,5-dicarboxylic Acid. Twenty-one grams (0.044 mol) of 2,5-dicarbethoxy-5-tetradecyldioxeno[2,3-*c*]thiophene was hydrolyzed by refluxing in 150 mL of 10% KOH for 12 h. After the mixture cooled to room temperature, a solid was filtered off and the filtrate added dropwise into 500 mL of 0.1 M HCl. A milky white precipitate was collected by vacuum filtration, washed with copious amounts of water, and oven-dried. Yield = 7.2 g (39%). Anal. Calcd: C, 61.95; H, 8.03; S, 7.50. Found: C, 59.04; H, 7.61; S, 7.87. ^{1}H-NMR (δ, ppm, TMS reference): 0.8−0.9, 1.18−1.6, 3.95−4.45, 13.1. ^{13}C-NMR: 14.84, 23, 25.19, 29.51, 29.63, 29.69, 29.80, 29.87, 29.96, 30.59, 32.22, 68.42, 74.65, 112.37, 112.5, 145.51, 145.76, 162.64. MS: molecular ion peak, 426 amu; base peak, 55 amu.

5-Octyldioxeno[2,3-*c*]thiophene. A mixture of 5-octyldioxeno[2,3-*c*]thiophene-2,5-dicarboxylic acid (1 g, 3 mmol) and 15% by mole of copper chromite, as a catalyst, were placed in a 500 mL 1NRBF with 100 mL of freshly distilled quinoline and heated to 150 °C for 24 h. After the mixture cooled to room temperature, 100 mL of pentane was added, the mixture was stirred, and the catalyst residue was filtered off through Celite. The quinoline was washed from the organic filtrate by repeated washing with 1 M HCl until the pH values of the aqueous layers were acidic. The organic layer was washed with 1 M $NaHCO_3$ and water until the pH became neutral. The organic layer was dried with anhydrous $CaCl_2$ and concentrated, and flash chromatography yielded a pale yellow liquid. Yield = 0.56 g (87%). Anal. Calcd: C, 66.01; H, 8.70; S, 12.57. Found: C, 66.10; H, 8.56; S, 12.11. ^{1}H-NMR (δ, ppm, TMS reference): 0.883 (t), 1.2−1.8, 3.8−4.2, 6.3. ^{13}C-NMR: 14.1, 22.65, 24.98, 29.21, 29.20, 29.40, 29.46, 30.66, 31.83, 68.47, 73.79, 99.20, 99.24, 141.72, 142.21. MS: molecular ion and base peak at 255.

5-Tetradecyldioxeno[2,3-*c*]thiophene. A mixture of 5-tetradecyldioxeno[2,3-*c*]thiophene-2,5-dicarboxylic acid (1 g, 2.3 mmol) and 15% by mole of copper chromite, as a catalyst, was placed in a 500 mL 1NRBF with 100 mL of freshly distilled quinoline and heated to 150 °C for 24 h. After the mixture cooled to room temperature, 100 mL of pentane was added, the mixture was stirred, and the catalyst residue was filtered off through Celite. The quinoline was washed from the organic filtrate by repeated washing with 1 M HCl until the pH values of the aqueous layers were acidic. The organic layer was washed with 1 M $NaHCO_3$ and water until the pH became neutral. The organic layer was dried with anhydrous $CaCl_2$ and concentrated, and flash chromatography yielded a whitish gray solid. Yield = 0.3 g (38%). Anal. Calcd: C, 70.97; H, 10.12; S, 9.4. Found: C, 71.08; H, 10.31; S, 7.87. ^{1}H-NMR

(δ, ppm, TMS reference): 0.88 (t), 1.2−1.7, 3.7−4.2, 6.29. ^{13}C-NMR: 15.2, 22.6, 22.7, 25.0, 29.2, 29.3, 29.4, 29.42, 29.44, 29.5, 29.7, 30.65, 31.8, 31.9, 68.2, 74.0, 99.8, 99.9, 142.0, 142.5. MS: molecular ion peak, 338 amu; base peak, 55 amu.

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