Conducting Poly(3,4-alkylenedioxythiophene) Derivatives as Fast Electrochromics with High-Contrast Ratios

Anil Kumar, Dean M. Welsh, Mark C. Morvant, Fabienne Piroux,
Khalil A. Abboud, and John R. Reynolds*

Department of Chemistry, Center for Macromolecular Science and Engineering,
University of Florida, Gainesville, Florida 32611

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A series of alkyl-substituted and unsubstituted poly(3,4-alkylenedioxythiophene)s were synthesized electrochemically using 3,4-alkylenedioxythiophene derivative monomers where either the size of the alkylenedioxy ring or the nature of the pendent group was varied. The specific systems studied include 3,4-ethylenedioxythiophene (EDOT), 2-methyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (EDOT-Me), 2-tetradecyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (EDOT-$C_{14}H_{29}$), 2-phenyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (EDOT-Ph), 3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (ProDOT), 3-methyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (ProDOT-Me), 2,3,4,5-tetrahydrothieno[3,4-*b*][1,4]dioxocine (BuDOT), and 5,10-dihydrobenzo-[*f*]thieno[3,4-*b*][1,4]dioxocine (BuDOT-Xyl). Optoelectrochemical experiments revealed that the nature of the substitution on the polymers had little effect on the extent of conjugation of the backbone as evidenced by electronic band gaps for all polymers of approximately 1.7 eV (730 nm). These electrochromic polymers switch from a relatively transmissive light green in the oxidized form to an opaque dark blue in the reduced form, with the highest electrochromic contrast ratios accessible for PBuDOT and PEDOT-$C_{14}H_{29}$. Multiple switching studies monitoring the electrochromic contrast showed that ca. 300 nm thick polymer films could be fully switched between their reduced and oxidized forms in 0.8−2.2 s with $\Delta\%T$ of 44−63%. In situ conductivity studies carried out on relatively thick polymer films (2.7−9.5 μm) deposited between large gap (200 μm) lateral growth electrodes demonstrated the low-potential turn-on for these materials, and maximum conductivities of 0.2−12.1 S/cm were attained.

Introduction

There is a great deal of interest in new electrochromic (EC) materials which exhibit rapid response times, long-term stability, and high $\Delta\%T$ (where T is the transmittance).[1] Much of the recent electrochromic device research has been based on inorganic EC materials.[1−5] Since these materials are often difficult to process and can have slow response times, there is a need for a broader variety of electrochromic materials. Recently, redox active conjugated and conducting polymers have attracted attention as EC materials as they have structurally controllable optical properties, can be electrodeposited to highly electroactive films, and some forms are processable from solution. Of the candidate polymers for electrochromics, poly(3,4-ethylenedioxythiophene) (PEDOT) has a low oxidation potential allowing it to easily switch between states, and in its oxidized and conducting form, it is significantly more stable to air exposure and elevated temperature conditions relative to other polythiophenes.[6,7] In addition to the electrochemical properties, PEDOT exhibits a relatively low optical absorption through the visible region and a high conductivity (200 S/cm), making it useful as a conductive transparent coating material.[8−10]

In our laboratory, we have been investigating the electrochromic properties of PEDOT and other EDOT-containing polymers.[11−15] By controlling the extent of

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(1) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, 1995.

(2) Bohnke, O.; Rezrazi, M.; Bohnke, V. C.; Rousselot, G. C.; *Solar Energy Mater. Solar Cells* **1992**, *25*, 361.

(3) Monk, P. M. S.; Chester, L. S. *Electrochim. Acta* **1993**, *38*, 1521.

(4) Thomas, G. R.; Owen, J. R. *Solid State Ionics* **1992**, 53−56, 513.

(5) Chang, I. F. *Non-Emmissive Electrooptic Displays*; Knetz, Von Willisen, Eds.; Plenum Press: New York, 1976; p 155.

(6) (a) Jonas, F.; Heywang, G.; Schidtberg, W. Ger. Offen. DE 3,-813,589, 1989. (b) Jonas, F.; Heywang, G.; Schidtberg, W.; Heinze, J.; Dietrich, M. Eur. Pat. App. EP 339,340, 1989. (c) Jonas, F.; Heywang, G.; Schidtberg, W.; Heinze, J.; Dietrich, M. U.S. Patent No. 5,035,926, 1991.

(7) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.

(8) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganäs, O. *Polymer* **1994**, *35*, 1347.

(9) Gustafsson, J. C.; Liedberg, B.; Inganäs, O. *Solid State Ionics* **1994**, *69*, 145.

(10) Dietrich, M.; Heize, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *369*, 87.

(11) Sotzing, G. A.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1995**, 703.

(12) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.

(13) Sankaran, B.; Reynolds, J. R. *Macromolecules* **1997**, *30*, 2582.

(14) (a) Reddinger, J. L.; Sotzing, G. A.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1996**, 1777. (b) Sotzing, G. A.; Reddinger, J. L.; Katritzky, A. R.; Soloducho, J.; Musgrave, R.; Steel, P. J.; Reynolds, J. R. *Chem. Mater.* **1997**, *9*, 1578.

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conjugation in a series of bis(2-EDOT)arylenes, we have been able to prepare a series of electrochromic polymers of any color. We have also shown that PEDOT can be used as a cathodically coloring polymer in dual polymer electrochromic devices that have both transmissive color neutral and absorptive highly colored states.[15]

To obtain a soluble and processable form of PEDOT, aqueous dispersions with polystyrene sulfonic acid have been made available.[16] We have shown that solubility can be induced in both the reduced and oxidized forms of alkyl derivatized PEDOTs and that films could be directly prepared from these solutions.[17] Recently the effect of alkyl group substitution on the optical and electrical properties of PEDOT and PEDOT vinylenes was studied.[18] Dietrich et al.[10] have compared the electrochemical and optical properties of PEDOT and poly(3,4-propylenedioxythiophene) (PProDOT). However, to date there are no reports available in the literature on a systematic study of the structure–electrochromic property relationships in poly(3,4-alkylenedioxythiophenes). In this paper, we report the effect of the size of the alkylenedioxy ring and the nature of pendant groups on the optical, electronic, and conductive properties of a series of poly(3,4-alkylenedioxythiophenes).

Experimental Section

Materials. 2,5-Dicarbethoxy-3,4-dihydroxythiophene (**1**) and the monomer 2-tetradecyl-2,3-dihydrothieno[3,4-*b*][1,4]-dioxine (**4c**) were synthesized as we reported previously.[13] EDOT (Bayer) was purified by distillation under reduced pressure. Tetrabutylammonium perchlorate (TBAP) was purified by recrystallization from ethyl acetate. Acetonitrile (ACN) was dried and distilled over calcium hydride under argon. Anhydrous *N*,*N*-dimethylformamide (DMF), anhydrous propylene carbonate (PC), and quinoline were purchased from Aldrich Chemical and used as received. Indium tin oxide (ITO)-coated glass plates were purchased from Delta Technologies.

Equipment. NMR spectra were obtained using a Varian Gemini-300 or a Varian XL-300 spectrometer. Mass spectrometry was carried out on a Finnigan MAT 95Q mass spectrometer. Elemental analysis was accomplished at Robertson Microlit Laboratories, Inc. The electrochemical studies were carried out using an EG&G PAR Model 273 potentiostat/galvanostat with Ag/Ag$^+$ as the reference electrode, a platinum button or an ITO coated glass plate as the working electrode, and platinum foil as the counter electrode in 0.1 M TBAP/ACN. Optoelectrochemical spectroscopy was carried out on a Varian Cary 5E UV–vis–near-infrared (NIR) spectrophotometer. Electropolymerization on large gap lateral growth electrodes (LG-LGEs) and in situ conductivity measurements were performed using a Pine Instrument Co. bipotentiostat Model AFCBP1. During electrochemical experiments, all electrolytes were purged with argon prior to use, and an argon blanket was retained over the cell. Film thicknesses were measured using a Sloan Dektak II profilometer.

In Situ Conductivity Measurements.[19] Polymer films were electrosynthesized potentiostatically from a 10 mM solution of monomer in 100 mM Li(CF$_3$SO$_2$)$_2$N/PC. The LG-LGEs were coated with a 1000 Ω graphite bridge and placed in an electrochemical cell along with a Cu mesh counter electrode and a Ag/Ag$^+$ (10 mM AgNO$_3$/100 mM TBAP/ACN) reference electrode. Working electrode 1 (WE1) was set at 1.150 V and working electrode 2 (WE2) was set at 1.145 V vs Ag/Ag$^+$. The polymer was allowed to deposit for 1 h while the potentials at WE1 and WE2 were switched every 10 min to ensure even deposition of polymer. The polymer-coated LG-LGEs were then washed with monomer-free electrolyte solution and stored wet prior to conductivity measurements.

Table 1. Crystallographic Data

	ProDOT	EDOT-Ph
Crystal Data (298 K)		
a, Å	8.1108(2)	9.1090(1)
b, Å	10.2518(3)	16.8237(4)
c, Å	8.6934(1)	6.6466(1)
β, deg	90.73(1)	92.774(1)
V, Å^3	722.06(3)	1017.42(3)
d_{calc}, g cm^{-3} (298 K)	1.437	1.425
empirical formula	$C_7H_8O_2S$	$C_{12}H_{10}O_2S$
formula wt, g	156.19	218.26
crystal system	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*
Z	4	4
F(000), electrons	328	456
crystal size, (mm^3)	0.38 × 0.28 × 0.17	0.20 × 0.19 × 0.13
Data Collection (298 K)		
radiation, λ (Å)	Mo Kα, 0.71073	
mode	ω-scan	
scan width & rate	0.3 deg/frame & 30 s/frame	
2θ range, deg	3–55	3–55
range of *hkl*	$-10 \le h \le 9$	$-12 \le h \le 12$
	$-13 \le k \le 7$	$-23 \le k \le 19$
	$-11 \le l \le 11$	$-8 \le l \le 7$
total reflections measured	4957	6895
unique reflections	1648	2331
absorption coeff μ(Mo Kα), mm^{-1}	0.378	0.291
min & max transmission	0.713 & 0.952	0.973 & 0.732
Structure Refinement		
S, goodness-of-fit	1.084	1.052
reflections used	1468, $I > 2\sigma(I)$	1871, $I > 2\sigma(I)$
no. of variables	124	177
R, wR^a (%)	2.78, 6.57	4.94, 8.75
R_{int} (%)	2.28	2.97
max shift/esd	0.001	0.001
min peak in diff Four. map (e Å^{-3})	−0.30	−0.21
max peak in diff Four. map (e Å^{-3})	0.28	0.57

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2,0) = 2F_c^2]/3$.

For the offset potential scans and in situ conductivity measurements, the polymer-coated LG-LGE was placed in an electrochemical cell along with a Cu mesh counter electrode and a Ag/Ag$^+$ reference electrode in monomer-free electrolyte solution. The offset potential sweep was obtained by setting an offset potential of 50 or 180 mV between WE1 and WE2 on the bipotentiostat. The polymer was cycled at 10 mV/s from −1.0 to +1.0 V while the drain current (i_D) vs potential was recorded. The in situ conductivity was measured by setting the potential at WE1 at a static potential while the potential at WE2 was cycled ±50 mV from WE1 and the drain current vs potential recorded. The current/voltage relationship allowed determination of the resistance of the polymer device at the potential of WE1 which was then converted to conductivity. This process was repeated over the desired potential range to show the relationship between in situ conductivity and applied potential.

X-ray Crystallography: Data Collection, Structure Solution, and Refinement. Basic X-ray crystallographic data for ProDOT and EDOT-Ph are shown in Table 1. A more extensive listing of data is contained in the Supporting Information.

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(15) Sapp, S. A.; Sotzing, G. A.; Reddinger, J. L.; Reynolds, J. R. *Adv. Mater.* **1996**, *8*, 808.

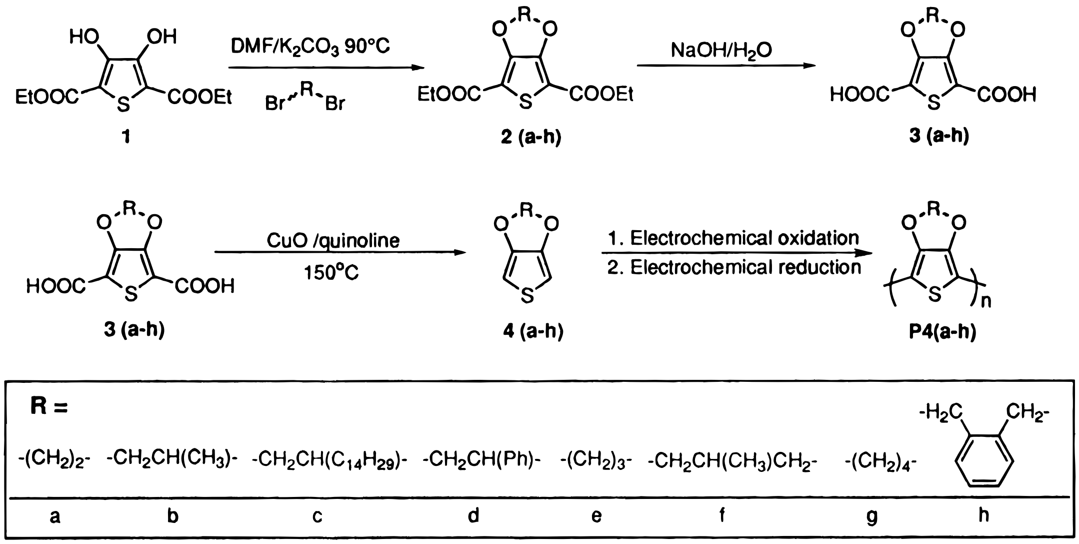
(16) Jonas, F.; Krafft, W.; Eur. Pat. App. EP 440,957, 1990.

(17) Kumar, A.; Reynolds, J. R. *Macromolecules* **1996**, *29*, 8551.

(18) Havinga, E. E.; Mutsaers, C. M. J.; Jenneskens, L. W. *Chem. Mater.* **1996**, *8*, 769.

(19) Morvant, M. C.; Reynolds, J. R. *Synth. Met.* **1998**, *92*, 57.

Scheme 1



Both structures were solved by the direct methods in *SHELXTL5* and refined using full-matrix least-squares on F^2.[20] The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were located in difference Fourier maps and refined without constraints. For ProDOT, 124 parameters were refined in the final cycle of refinement using 1468 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.78 and 6.57, respectively. And for EDOT-Ph, 177 parameters were refined in the final cycle of refinement using 1871 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.68 and 8.23, respectively.

Synthetic Procedures. *2,5-Dicarbethoxy-3,4-alkylenedioxythiophenes* (**2b,d–h**). In a general synthesis, 1 equiv of 2,5-dicarbethoxy-3,4-dihydroxythiophene was stirred at 90 °C under argon for 48 h in the presence of 1 equiv of corresponding dibromoalkane and 3 equiv of anhydrous K_2CO_3 in anhydrous DMF. The resultant mixture was cooled to room temperature, poured into an excess of water, and extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous magnesium sulfate before removing ether at reduced pressure to obtain the corresponding product. All compounds gave appropriate analyses by ^{1}H and ^{13}C NMR and elemental analysis. Specific results are reported as Supporting Information.

2,5-Dicarboxy-3,4-alkylenedioxythiophenes (**3b,d–h**). One equivalent of 2,5-dicarbethoxy-3,4-alkylenedioxythiophene was stirred at 90 °C under argon for 10 h with 3 equiv of NaOH in water. The resulting solution was cooled to room temperature and acidified with 1 M HCl to precipitate a white solid product. The product was filtered, washed with water, and dried under vacuum. All compounds gave appropriate analyses by ^{1}H and ^{13}C NMR and elemental analysis. Specific results are reported as Supporting Information.

3,4-Alkylenedioxythiophenes (**4b,d–h**). One equivalent of 2,5-dicarboxy-3,4-alkylenedioxythiophene was heated at 150 °C with 17 mol % of copper chromite in quinoline for 20 h under argon. After cooling, the mixture was filtered through Celite and poured into an excess of 1 M HCl. The product was extracted with ether, washed with 1 M HCl until the washings were acidic, and washed with water. Ether was removed under reduced pressure after drying the organic layer over anhydrous magnesium sulfate. The products obtained were purified by flash chromatography. All compounds gave appropriate analyses by ^{1}H and ^{13}C NMR, high-resoltion mass spectrometry (HRMS), and elemental analysis. Specific results are reported as Supporting Information.

Results and Discussion

Monomer Synthesis. The synthesis of the monomers is outlined in Scheme 1. 3,4-Dihydroxy-2,5-carboethoxythiophene (**1**) was synthesized from thiodiglycolic acid as described previously.[13] Etherification of **1** with the appropriate dibromo derivative in DMF/K_2CO_3 at 90 °C yielded the corresponding ring-closed products. These were then saponified in NaOH/H_2O followed by decarboxylation with CuO in quinoline to yield the final monomers. The monomers were purified by flash chromatography using CH_2Cl_2 as eluent. All of the monomers gave appropriate analyses by ^{1}H and ^{13}C NMR, elemental analysis, GC, and HRMS. Differing the substitution and alkylenedioxy ring size affects the physical properties of the monomers. EDOT, EDOT-Me, and BuDOT are liquids at room temperature, while EDOT-$C_{14}H_{29}$, EDOT-Ph, ProDOT, and BuDOT-Xyl are solids. As expected, when the molecular weight is increased significantly relative to EDOT, the monomers are solids. Interestingly, when the ring size is increased from two to three carbons, from EDOT to ProDOT and ProDOT-Me, nicely crystalline solids were obtained. The crystallization of ProDOT can be attributed to strong intermolecular interactions between oxygen (O1 and O1A) and the adjacent thienyl hydrogen (H1 and H1A) as shown by the dimer crystal structure in Figure 1.

The crystal structure for the monomer unit of EDOT-Ph is shown in Figure 2. In this instance, there are no intermolecular interactions. Of interest here is the fact that the phenyl substituent is nearly (73.8°) orthogonal to the thiophene ring, suggesting that the phenyl group will serve to separate polymer chains in the solid state.

Electropolymerization. The repeated scan electropolymerization behavior of a 10 mM solution of all the monomers **4(a–h)** was examined in 0.1 M TBAP/ACN. The representative electrochemical growth and the scan rate dependence for **P4d** (PEDOT-Ph) and **P4e** (PProDOT) are shown in Figures 3 and 4, respectively. The monomer oxidation at the bare electrode starts at 0.9 V and peaks ($E_{p,m}$) at 1.1 V vs Ag/Ag$^+$ in all cases. With repeated scanning, a reversible redox process quickly grows in with an $E_{1/2}$ at −0.1 V. It is evident that the polymer redox develops quite rapidly and that

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[20] Sheldrick, G. M. *SHELXTL5*; Siemens Analytical Instrumentation, Madison, WI, 1995.

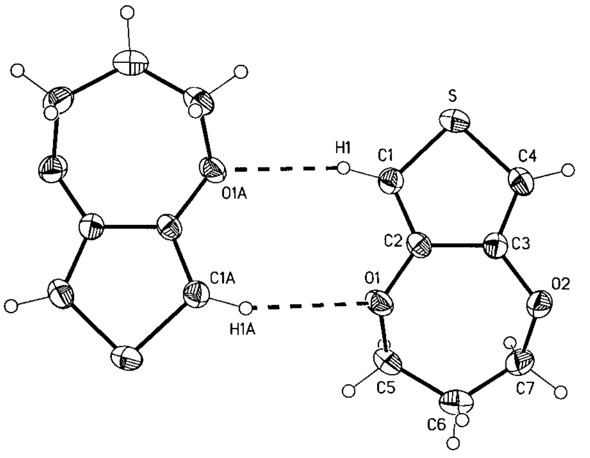

Figure 1. View of two adjacent molecules and atom labeling of the crystal structure of ProDOT.

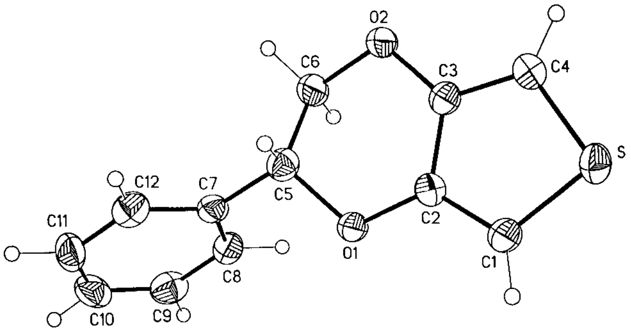

Figure 2. Perspective view and atom labeling of the crystal structure of EDOT-Ph.

the monomers are polymerizing very efficiently to form highly electroactive polymers **P4(a−h)**. The polymer films were then washed with monomer-free electrolyte solution, and the scan rate dependence of the polymer redox was investigated. A linear relationship was found between the peak current and scan rate in all cases, indicating that the electroactive polymer films are well-adhered and the redox processes are nondiffusion limited. The only difference between PProDOT polymer electrochemistry and other derivatives is that PProDOT has sharper and better resolved redox peaks in the cyclic voltammogram as compared to the broad peaks observed for the other derivatives, similar to PEDOT-Ph (Figure 3).

Optoelectrochemistry. For optoelectrochemical studies, polymer films were electrochemically deposited from a 10 mM solution of the monomers in 0.1 M TBAP/ACN on ITO-coated glass plates at a constant potential of 1.15 V vs Ag/Ag$^+$. The films were washed with monomer-free electrolyte solution before studying the optoelectrochemical properties. A series of UV−vis−NIR spectra were obtained as a function of applied potential and confirmed the typical bipolaronic nature of the charge carriers. The optoeletrochemical spectra for PEDOT and PEDOT-Ph are shown in Figures 5 and 6, respectively. The neutral form of the polymers shows a distinct π to π^* transition with a band gap onset of 1.7 eV (775 nm) and a peak at 2.0 eV (625 nm). Stepwise oxidation of the polymer shows reduction in absorbance throughout the visible region as the color changes from a dark blue absorbing state (fully reduced form) to a highly transmissive state (oxidized form). The interesting feature to note in Figure 6 is the growth of a peak at 1.25 eV. The intensity of this peak continuously increases for PEDOT as the polymer oxidizes. However, in the case of PEDOT-Ph and **P4f** (PProDOT-Me),the peak at 1.25 eV grows during the initial oxidation of the polymer but subsequently decreases in intensity upon full oxidation of the polymer. This decrease in intensity of the 1.25 eV peak increases the transmissivity throughout the visible region (1.7−3.0 eV) as the near-infrared tail is eliminated. This results in higher contrast electrochromic material and gives thin films of the polymers a more color neutral appearance. This type of behavior is similar to what has been observed for **P4c** (PEDOT-$C_{14}H_{29}$) and by Havinga with PEDOT-C_6H_{13}.[13,18] The optoelectrochemical spectra of PProDOT is shown in Figure 7. In this case, and in the cases of **P4g** (PBuDOT) and **P4h** (PBuDOT-Xyl), the optoelectrochemical spectra are similar to that of PEDOT with respect to the growth of the peak at 1.25 eV. However, with PProDOT the interband transition is split into two distinct peaks at 2.0 and 2.2 eV. This splitting also occurs in PEDOT-$C_{14}H_{29}$ and can be attributed to vibronic coupling which suggests a high degree of regularity along the polymer backbone.[21]

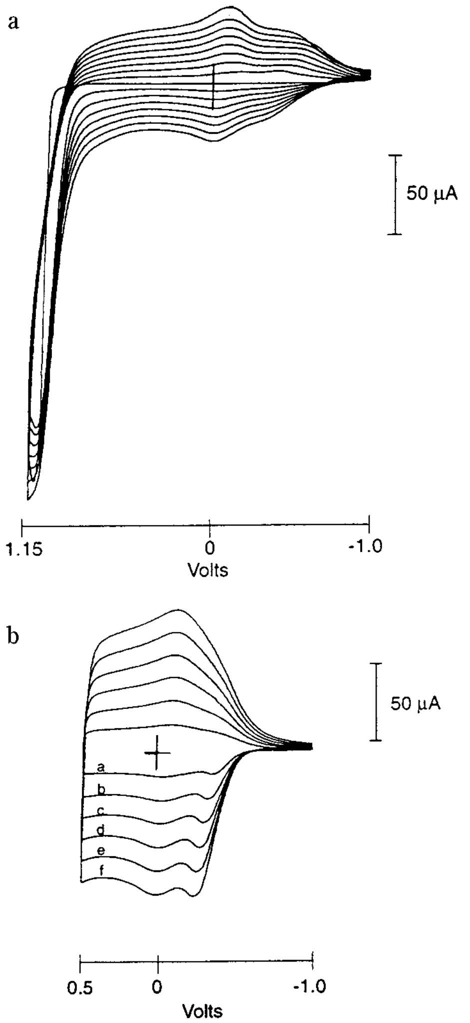

Figure 3. (a) Repeated potential scan electropolymerization of 4d (EDOT-Ph) at 100 mV/s in 0.1 M TBAP/ACN. (b) Scan rate dependence of P4d (PEDOT-Ph): (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, (f) 300 mV/s.

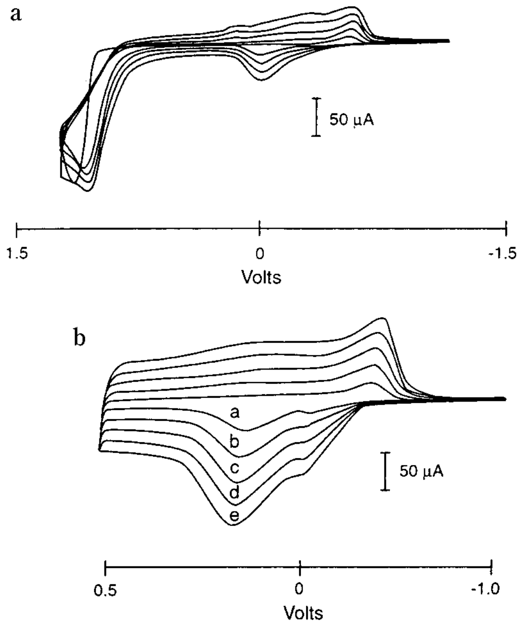

Figure 4. (a) Repeated potential scan electropolymerization of 4e (PProDOT) at 100 mV/s in 0.1 M TBAP/ACN. (b) Scan rate dependence of P4e (PProDOT): (a) 50, (b) 100, (c) 150, (d) 200, (e) 250 mV/s.

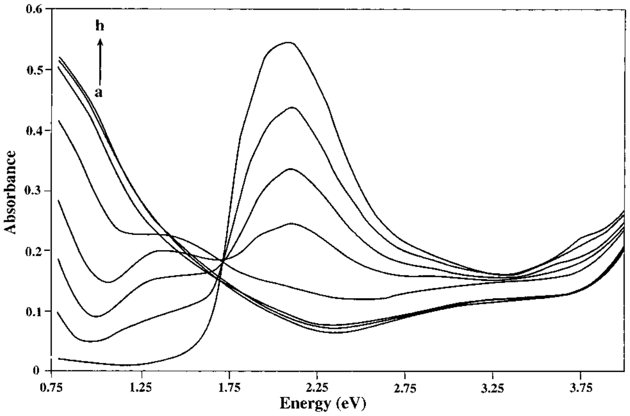

Figure 5. Optoelectrochemical spectra for PEDOT as a function of applied potential between −0.3 and 1.2 V in 0.1 M TBAP/ACN: (a) −0.3V, (b) −0.1, (c) 0, (d) +0.1, (e) +0.2, (f) +0.3, (g) +0.6, (h) +1.2 V.

Optical Switching Rate Studies. For optical switching studies, polymer films were electrochemically deposited from a 10 mM solution of monomer in 0.1 M TBAP/ACN on ITO-coated glass plates at a constant potential of 1.15 V. The films were then washed with monomer-free electrolyte solution and dried before measuring the thickness. For each polymer, film thickness (as determined by profilometry) was determined to be linearly proportional to charge density (four to five samples for each polymer) in all cases. Change in film thickness as a function of charge density (d*t*/d*Q*) values are listed in Table 2. As can be seen, all of the polymers except PEDOT-$C_{14}H_{29}$ have comparable thickness for a given charge density while PEDOT-$C_{14}H_{29}$ is about six times as thick for a given charge density. It is likely that the long alkyl chains hold the conjugated backbones apart from one another, leading to a more expanded morphology.

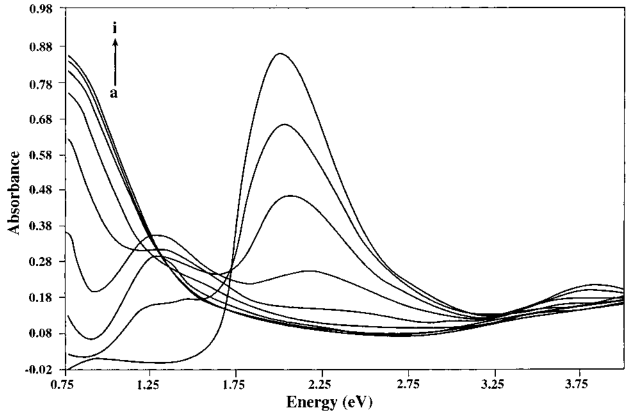

Figure 6. Optoelectrochemical spectra for PEDOT-Ph as a function of applied potential between −0.3 and 1.5 V in 0.1 M TBAP/ACN: (a) −0.3, (b) −0.1, (c) +0.1, (d) +0.3, (e) +0.5, (f) +0.7, (g) +1.0, (h) +1.3, (i) +1.5.

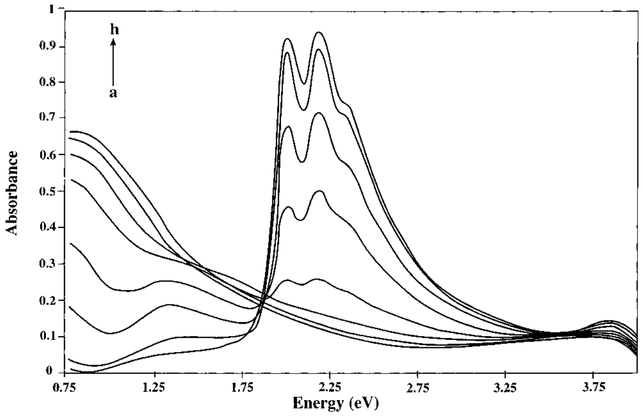

Figure 7. Optoelectrochemical spectra for PProDOT as a function of applied potential between −0.3 and 1.5 V in 0.1 M TBAP/ACN: (a) −1.0, (b) −0.2, (c) 0, (d) +0.1, (e) +0.2, (f) +0.3, (g) +0.5, (h) +1.0 V.

Table 2. Electrochromic Properties and in Situ Conductivity Results for Poly(3,4-alkylenedioxythiophene) Derivatives

polymer	dt/dQ[a]	Δ%T[b]	switching time (s)[b]	in situ conductivity maximum (S/cm)
PEDOT	5.2	44	2.2	8.6
PProDOT	6.0	54	2.2	12.1
PBuDOT	5.5	63	1.3	0.2
PEDOT-$C_{14}H_{29}$	28.7	63	0.8	4.5
PEDOT-Ph	5.8	45	0.8	1.2

[a] Change of film thickness (nm) as a function of charge density (mQ/cm^2). [b] As determined by optical switching studies (see text for details).

For optical switching studies, polymer films of constant thickness (ca. 300 nm) were washed with monomer-free electrolyte solution and switched by repeated potential steps between their reduced (−1.0 V) and oxidized (+1.0 V) states. In these studies, the Δ%T of the polymer films were monitored as a function of time at a constant wavelength near $\lambda_{\max}$ for each of the polymers (590 nm). The switching times were optimized to yield the maximum transmittance contrast as shown in Table 2. To allow a comparison of the systems, the results of these switching studies for PEDOT, PBuDOT, and PEDOT-Ph are shown in Figures 8, 9, and 10, respectively. In the case of PEDOT and PProDOT, the switching time to allow maximum electrochromic contrast was found to be 2.2 s, whereas it was found to be

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(21) Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl. F. *J. Polym. Sci.* **1987**, *25*, 1071.

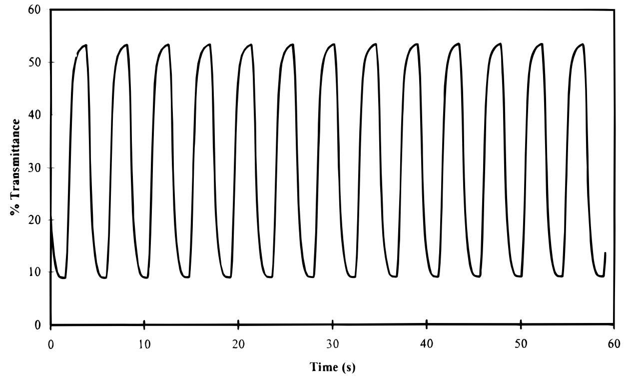

Figure 8. Electrochromic switching, optical absorbance change monitored at 590 nm for PEDOT in 0.1 M TBAP/ACN.

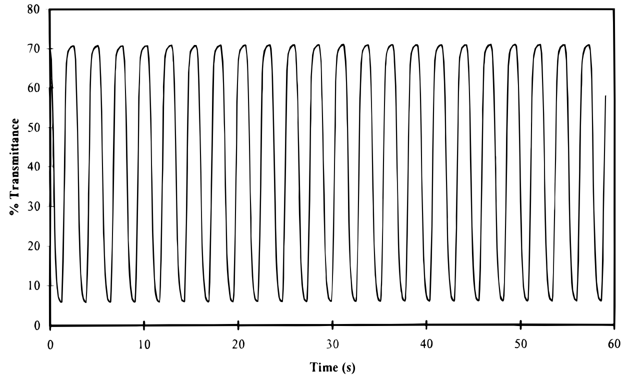

Figure 9. Electrochromic switching, optical absorbance change monitored at 590 nm for PBuDOT in 0.1 M TBAP/ACN.

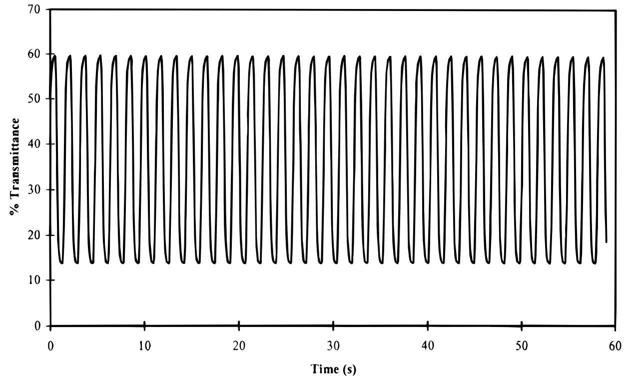

Figure 10. Electrochromic switching, optical absorbance change monitored at 590 nm for PEDOT-Ph in 0.1 M TBAP/ACN.

1.3 s for PBuDOT. In addition, PEDOT-$C_{14}H_{29}$ and PEDOT-Ph switching times were found to be even faster at 0.8 s. Reviewing these results, it is evident that increasing the ring size or size of the substituent on the alkylenedioxy bridge reduces the switching time.

These results also show that the optical contrast ($\Delta\%T$) increases with the size of the alkylenedioxy ring from 44% for PEDOT to 54% for PProDOT to 63% for PBuDOT. The $\Delta\%T$ for PEDOT-$C_{14}H_{29}$ and PEDOT-Ph was found to be 63% and 45%, respectively. As with the switching times discussed above, increasing the ring size or size of the substituent on the alkylenedioxy bridge enhances the electrochromic contrast. Many electrochromic applications require high-contrast ratios allowing devices to be prepared that are opaque in one state while being highly transmissive in the other. For these, PBuDOT and PEDOT-$C_{14}H_{29}$ are the best candidate polymers from this study. In fact, visual observation of these films during switching show them to perform significantly better than PEDOT with a neutral gray/green color that is more transmissive than the parent polymer. In addition, the monomer BuDOT is significantly easier to synthesize than the long chain alkyl derivative, indicating BuDOT to be of further interest for future work in our laboratory.

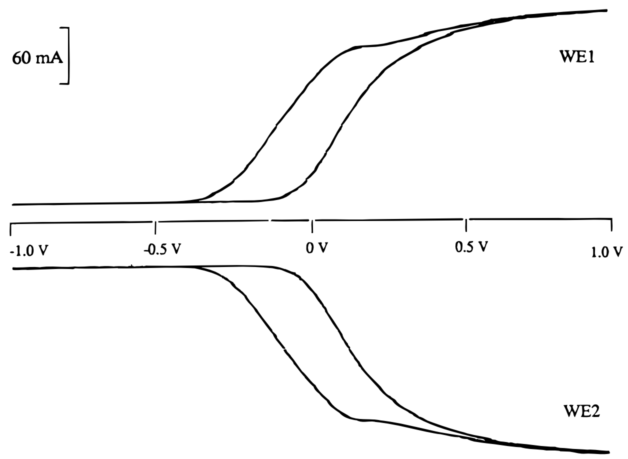

Figure 11. Offset potential scan of PProDOT with working electrode 2 (WE2) offset by −50 mV form working electrode 1 (WE1).

In Situ Conductivity. Figure 11 shows the offset potential scan of a PProDOT device and is representative of the offset potential scans obtained for the other polymers. At −1.0 V, the polymer is in its insulating state and exhibits a low drain current (<5 μA) between WE1 and WE2. As the applied potential becomes more positive, the polymer is oxidized, and the drain current begins to increase until a maximum drain current is obtained. It can be seen that the current responses observed at WE1 and WE2 are identical (though reversed in sign). This is indicative of good electronic communication between the two electrodes as the film was laterally contacted. Unsymmetrical current responses were occasionally observed, indicating poor lateral growth characteristics, and the devices were not examined further. Devices that exhibited reproducible and symmetric current responses were then used for in situ conductivity measurements.

Figure 12 shows the in situ conductivity of the polymers vs applied potential as measured using the procedure described by Wrighton.[22-24] The low but reproducible conductivity of the devices at low potentials (−1.0 V vs Ag/Ag^+) of ca. 10^{-4} S/cm were a result of the graphite bridge that had been deposited on the LG-LGEs to facilitate lateral polymer growth. Upon oxidation, the elevated device conductivities are a result of the more highly conductive polymers which are several orders of magnitude more conducting than the graphite bridge deposited. The maximum in situ conductivities of PEDOT and PProDOT were about 10 S/cm, while the in situ conductivities of the substituted polymers, PEDOT-$C_{14}H_{29}$ and PEDOT-Ph, were slightly lower at

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(22) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.

(23) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 6, 7389.

(24) Thackery, J. W.; White, H. S.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 5133.

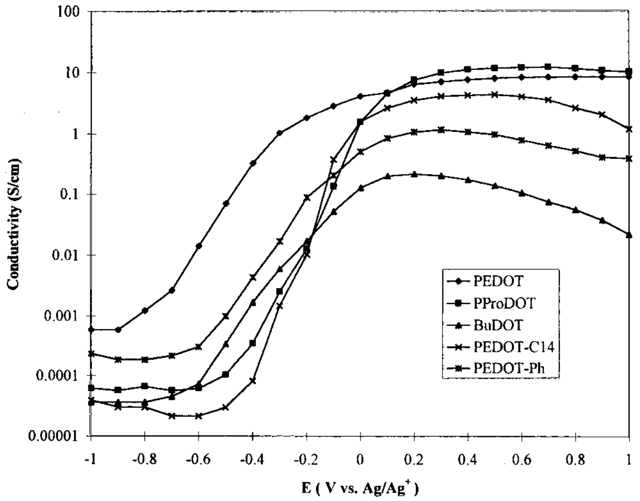

Figure 12. In situ conductivity vs applied potential for the poly(3,4-alkylenedioxythiophene) derivatives.

about 3 S/cm. Throughout these experiments, we find that PProDOT exhibits a reproducibly higher conductivity than PEDOT. We attribute this to the fact that the ProDOT monomer is a crystalline solid and could be easily obtained, stored, and handled in a highly pure state. EDOT, on the other hand, requires distillation for purification and, as a liquid, is slightly reactive allowing the formation of small amounts of impurities during storage. PBuDOT showed the lowest maximum in conductivity at 0.2 S/cm. While the parent PEDOT turned on its conductivity at the lowest potential, the substituted EDOT polymers had the smallest potential difference (ca. 0.5 V) for conductivity switching with PEDOT-$C_{14}H_{29}$, having a minimum conductivity at -0.5 V and a maximum conductivity near 0.2 V vs Ag/Ag$^+$.

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Supporting Information Available: Listings of anisotropic displacement parameters, hydrogen coordinates, and isotropic parameters are provided for ProDOT and EDOT-Ph along with an extensive listing of monomer characterization results (15 pages). Ordering information is given on any current masthead page.

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