

# Composite Coloration Efficiency Measurements of Electrochromic Polymers Based on 3,4-Alkylenedioxythiophenes

Carleton L. Gaupp,<sup>†</sup> Dean M. Welsh,<sup>†,‡</sup> R. David Rauh,<sup>§</sup> and John R. Reynolds<sup>\*,†</sup>

Center for Macromolecular Science and Engineering, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, and EIC Laboratories, Inc., 111 Downey Street, Norwood, Massachusetts 02062-2612

Received May 3, 2002. Revised Manuscript Received June 26, 2002

We report a method to measure the composite coloration efficiency of organic electrochromic polymers at 95% of the total optical density change measured at  $\lambda_{\max}$ . This practical method is useful for the comparison of organic polymers as well as inorganic electrochromic oxides and for gaining insights into the reasons for increased efficiencies in organic polymer systems. Three polymers from the family of the poly(3,4-alkylenedioxythiophenes) (PXdOTs) were chosen, due to their well-behaved electrochromic properties, to develop the tandem chronoabsorptometry/chronocoulometry method. Coloration efficiencies were measured by monitoring the amount of injected/ejected charge as a function of the change in optical density of the polymer film. The results of these experiments revealed a significant relationship between structure and coloration efficiency determined at  $\lambda_{\max}$  in organic polymers. Poly(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-*b*]dioxepine) (PProDOT-Me<sub>2</sub>) possessed the highest coloration efficiency (375 cm<sup>2</sup>/C) compared to poly(3,4-ethylenedioxythiophene) (PEDOT) (183 cm<sup>2</sup>/C) and poly(3,4-propylenedioxythiophene) (PProDOT) (285 cm<sup>2</sup>/C), due to a combination of larger changes in optical density at  $\lambda_{\max}$  and higher doping levels.

## Introduction

Conjugated organic polymers have received significant attention throughout the course of the past 2 decades, stemming not only from their high conductivities in the doped state but also from a variety of optoelectronic and redox properties.<sup>1</sup> One of these properties is electrochromism, which is defined as a reversible electromagnetic absorbance/transmittance change in response to an externally applied potential.<sup>2</sup> Several properties, crucial for the success of potential electrochromics (EC) for such device applications as electrochromic windows, mirrors, and displays, are embodied by organic polymer systems.<sup>3</sup> These include their rapid response times ( $\tau$ ), optical density change ( $\Delta OD$ ) (which can be measured as an absorbance change ( $\Delta A$ ), percent transmittance ( $\Delta \% T$ ) or luminance change ( $\Delta \% Y$ )), low power requirements, highly efficient color changes in response to applied potentials, and the

ability to structurally modify the monomer to achieve specific colors.

One such EC polymer that has been studied extensively, both by our research group<sup>4</sup> and by others,<sup>5</sup> is poly(3,4-ethylenedioxythiophene) (PEDOT, **1**). PEDOT is an electrically conducting polymer that is also inherently electrochromic. While providing conductivity in relatively transparent films was the initial driving force behind the development of PEDOT, its electrochromic properties have proven to be potentially useful as well. PEDOT is a cathodically coloring polymer, capable of repeated switching between the absorbing, neutral, and insulating state (dark blue/purple) and the highly transmissive, oxidatively doped, and conducting state (sky blue). Its conductivity resulted in PEDOT's application as an antistatic coating and subsequent commercial availability by way of an aqueous dispersion with poly(styrene sulfonate), PSS (as the charge-compensating polyelectrolyte).<sup>6</sup> This solution based form of PEDOT maintains the robust switching capabilities of its electrodeposited counterparts while eliminating the disadvantage of poor processibility.

\* To whom all correspondence should be addressed. E-mail: reynolds@chem.ufl.edu.

<sup>†</sup> University of Florida.

<sup>‡</sup> Permanent address: The Dow Chemical Co., Building 1702, Midland, MI 48674.

<sup>§</sup> EIC Laboratories, Inc.

(1) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.

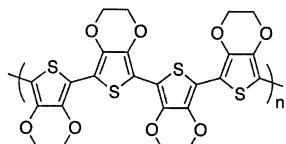
(2) (a) Verghese, M. M.; Ram, M. K.; Vardhan, H.; Malhorta, B. D.; Ashraf, S. M. *Polymer* **1997**, *38*, 1625. (b) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, Germany, 1995. (c) Bange, K.; Bambke, T. *Adv. Mater.* **1990**, *2*, 10.

(3) Reddinger, J. L.; Reynolds, J. R. *Advances in Polymer Science*; Wegner, G., Ed.; Springer-Verlag: Berlin, 1999; Vol. 145.

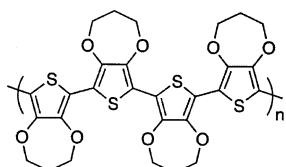
(4) (a) Kumar, A.; Reynolds, J. R. *Macromolecules* **1996**, *29*, 7629. (b) Sankaran, B.; Reynolds, J. R. *Macromolecules* **1997**, *30*, 2582. (c) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Adv. Mater.* **1997**, *9*, 795.

(5) (a) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116. (b) Pei, Q.; Zuccarello, G.; Ahlskong, M.; Inganäs, O. *Polymer* **1994**, *35*, 1347. (c) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481. (d) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (e) Heuer, H. W.; Wehrmann, R.; Kirchmeyer, S. *Adv. Funct. Mater.* **2002**, *12*, 89.

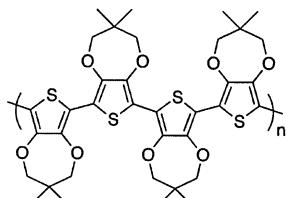
(6) (a) Gustafsson, J. C.; Liedberg, B.; Inganäs, O. *Solid State Ionics* **1994**, *69*, 145. (b) Dietrich, M.; Heize, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *387*, 369.



PEDOT, 1



PProDOT, 2

PProDOT-Me<sub>2</sub>, 3

PEDOT is but one polymer in a larger family of electrochromic materials known as the poly(3,4-alkylenedioxythiophenes) or PXDOTs.<sup>7</sup> PXDOTs, such as poly(3,4-propylenedioxythiophene) (PProDOT, **2**) and poly(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-*b*]dioxepine) (PProDOT-Me<sub>2</sub>, **3**), exhibit all of the aforementioned requirements for a successful electrochromic material that PEDOT possesses. The PXDOTs have subsecond response times for large  $\Delta OD$ ,  $\Delta\%T$  values that approach 75–80% at  $\lambda_{\max}$ , and exceptional switching stability, maintaining up to 60% of their optical response, even after several thousand deep double potential steps. It has been shown that by varying the substitution on the 3- and 4-positions of the PXDOTs, from ethylene (EDOT) to propylene (ProDOT) and dimethylpropylene (ProDOT-Me<sub>2</sub>), a decrease in response time and an increase in EC contrast at  $\lambda_{\max}$  between doped and neutral states is achieved.

Not only are the XDOTs able to form stable electrochromic homopolymers, but they are also easily functionalized at the 2-position to form multiring conjugated monomers that can be used to yield hybrid copolymers. These include substituted benzenes,<sup>8</sup> carbazoles,<sup>9</sup> and cyanovinylenes,<sup>10</sup> among others.<sup>11</sup> The result of these synthetic modifications is a wide range of colors as well as the ability to prepare soluble polymers for large area deposition. These physical and optical properties make

(7) (a) Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 896. (b) Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv. Mater.* **1999**, *11*, 1379.

(8) (a) Irvin, J. A.; Reynolds, J. R. *Polymer* **1998**, *39*, 2339. (b) Wang, F.; Wilson, M. S.; Rauh, R. D.; Schottland, P.; Thompson, B. C.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 2083.

(9) Sotzing, G. A.; Reddinger, J. L.; Katritzky, A. R.; Solodutto, J.; Musgrave, R.; Steel, P. J.; Reynolds, J. R. *Chem. Mater.* **1997**, *9*, 1578.

(10) Sotzing, G. A.; Thomas, C. A.; Steel, P. J.; Reynolds, J. R. *Macromolecules* **1998**, *31*, 3750.

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

the PXDOTs attractive as potential candidates for EC device applications and for use in the development of new methods for quantifying electrochromism.

The presence of electrochromism by itself is not sufficient when considering the role of polymers for the fabrication of EC devices, as the efficiency with which they switch is important as well. Inorganic electrochromic materials such as tungsten oxide ( $WO_x$ ) and iridium dioxide ( $IrO_2$ ) have been used extensively in EC device applications, due to their availability and cost.<sup>12</sup> These types of materials typically require larger amounts of charge, compared to organic polymers such as the PXDOTs, to achieve the same amount of color change, possibly due in part to fundamental differences in the energies and oscillator strengths in the associated electronic transitions.<sup>13</sup>

Spectroelectrochemistry has been widely used to assess the electronic structure and the nature of electrochromism in conducting polymers. *In situ* colorimetry has also been utilized to precisely map the colors associated with EC polymers.<sup>14</sup> Coloration efficiency (CE) measurements are another tool with which to study and better understand the EC phenomenon. The analysis of CE is important, yet the methods utilized to measure it have varied between research groups, making comparisons between systems difficult. CE ( $\eta$ ) is defined as the relationship between the injected/ejected charge as a function of electrode area ( $Q_d$ ) and the change in optical density,  $\Delta OD$ , at a specific dominant wavelength ( $\lambda_{\max}$ ) as illustrated by eq 1

$$\eta = \Delta OD(\lambda)/Q_d \quad (1)$$

where  $\Delta OD = \log[T_{ox}/T_{red}]$ .<sup>2,15</sup> The ideal material or device would exhibit a large transmittance change with a small amount of charge, giving rise to large CEs.

This quantity has been used extensively in the inorganic electrochromic literature where one of the redox states of the material is colorless. Measuring CE for organic polymers is equally important for comparative purposes as we look to determine how subtle changes in polymer structure effect the electrochromism. For example, while the interband transition of the PXDOTs is bleached during oxidative doping, there is a lower energy carrier band that tends to tail into the region of the initial band.<sup>7</sup> This complex behavior can reduce the overall composite CE as a truly bleached (nonabsorbing) state is never reached.

For comparison sake, CE values have been recorded for various inorganic and organic molecules, polymers, and devices. Granqvist has exhaustively reviewed the techniques and results of several researchers who have

(12) (a) Mortimer, R. J. *Chem. Soc. Rev.* **1997**, *26*, 147. (b) Rosseinsky, D. R.; Mortimer, R. J. *Adv. Mater.* **1997**, *13*, 783. (c) Granqvist, C. G. *Electrochim. Acta* **1999**, *44*, 3005. (d) Rauh, R. D. *Electrochim. Acta* **1999**, *44*, 3165.

(13) (a) Hyodo, K. *Electrochim. Acta* **1993**, *39*, 265. (b) Mortimer, R. J. *Electrochim. Acta* **1999**, *44*, 2971. (c) De Paoli, M.-A.; Casalbore-Miceli, G.; Girotto, E. M.; Gazotti, W. A. *Electrochim. Acta* **1999**, *44*, 2983.

(14) (a) Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. *Chem. Mater.* **2000**, *12*, 1563. (b) Brotherson, I. D.; Mudigonda, D. S. K.; Osborn, J. M.; Belk, J.; Chen, J.; Loveday, D. D.; Boehme, J. L.; Ferraris, J. P.; Meeker, D. L. *Electrochim. Acta* **1999**, *44*, 2993. (c) Mudigonda, D. S. K.; Meeker, D. L.; Loveday, D. C.; Osborn, J. M.; Ferraris, J. P. *Polymer* **1999**, *40*, 3407. (d) Boehme, J. L.; Mudigonda, D. S. K.; Ferraris, J. P. *Chem. Mater.* **2001**, *13*, 4469.

(15) Rauh, R. D.; Cogan, S. F. *Solid State Ionics* **1988**, *28–30*, 1707.

measured the CEs of a variety of inorganic oxide materials.<sup>16</sup> Amorphous tungsten oxide ( $\text{A-WO}_3$ ), which can be prepared by various techniques, yields CE values between 40 and 50  $\text{cm}^2/\text{C}$ .<sup>17</sup> The observed variations are due to film morphology and its effect on the coloration spectrum, since different deposition methods result in films of varying density. Also,  $\lambda_{\text{max}}$  for  $\text{M}_x\text{WO}_3$  (where M can be H, Li, Na, or K) films is not in the visible region, but rather in the NIR. For this reason, CE is typically measured at the steep leading edge of the absorption in the visible region, unlike organic polymers, where the  $\lambda_{\text{max}}$  values generally lie well within the visible region. Consequently, CE will vary greatly based on the selected wavelength. Another reason for varying values is that the CE for  $\text{WO}_3$  is linear for the initial part of the insertion reaction (where CE is usually measured) but then levels off at higher insertion levels. Iridium dioxide ( $\text{IrO}_2$ ), another popular inorganic material, exhibits a relatively flat CE of between 15 and 18  $\text{cm}^2/\text{C}$ .<sup>18</sup> Conducting polymers typically exhibit higher CE values than inorganic materials in the visible region. For example, poly(bithiophene) and poly(3-methylthiophene) electrosynthesized on ITO-coated glass slides give CE values of 110 and 240  $\text{cm}^2/\text{C}$ , respectively, at their  $\lambda_{\text{max}}$ .<sup>19</sup> CE values for complementary devices have also been recorded. A device consisting of poly(aniline) and tungsten trioxide with a gel electrolyte gives a CE value of 170  $\text{cm}^2/\text{C}$ .<sup>20</sup> Our group has reported on dual polymer devices using PEDOT and PEDOT- $\text{C}_{14}\text{H}_{29}$  as cathodically coloring polymers and poly[3,6-bis(2-(3,4-ethylenedioxythiophene))-*N*-alkylcarbazoles] as anodically coloring polymers. These devices exhibited very high coloration efficiencies of up to 1400  $\text{cm}^2/\text{C}$ .<sup>21</sup> Several other conjugated polymers have been studied that also possess high CE values.<sup>22</sup>

It is important to note that organic polymers possess many states while being doped. Polarons, bipolarons, and  $\pi$ -dimers all factor into the overall properties of organic EC polymers.<sup>23</sup> In addition, conformational changes occurring along the polymer backbone during doping (twisted aromatic form to a planar quinoidal form) are also important. Therefore, the task of measuring the coloration efficiency of such systems becomes complex. Factors such as doping levels and structure also become increasingly important when considering the *composite* coloration efficiency. Here, we use the term "composite coloration efficiency" to delineate the difference in the reported results with the more typically used slow measurement methods. The composite method captures the overall optical density change for a near complete switch and provides practical information for how an EC material will respond in a device upon switching between two extreme states. A problem lies in the ability to compare CE values between different types of materials when different methods to measure

(16) (a) Granqvist, C. G. *Handbook of Inorganic Electrochromic Materials*; Elsevier: Amsterdam, 1995. (b) Granqvist, C. G. *Sol. Energy Mater. Sol. Cells* **2000**, *60*, 201.

(17) Hitchman, M. L. *J. Electroanal. Chem.* **1977**, *85*, 135.

(18) Dautremont-Smith, W. C. *Displays* **1982**, *3*.

(19) Mastragostino, M.; Arbizzani, C.; Ferloni, P.; Marinangeli, A. *Solid State Ionics* **1992**, *53-56*, 471.

(20) Michalak, F.; Aldebert, P. *Solid State Ionics* **1996**, *85*, 265.

(21) Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 2101.

(22) Rauh, R. D.; Wang, F.; Reynolds, J. R.; Meeker, D. L. *Electrochim. Acta* **2001**, *46*, 2023.

CE are used. In this paper we present a general method for measuring the *composite* coloration efficiency of electrochromic polymers effectively and consistently by a tandem chronocoulometry/chronoabsorptometry experiment. This allows us to practically and quickly measure, and quantitatively compare, CE values for different systems.

## Results and Discussion

**Tandem Chronoabsorptometry/Chronocoulometry Experiment.** Three 3,4-alkylenedioxythiophene polymers were selected to carry out our *composite* coloration efficiency experiments to further probe the structure/property relationships in electrochromic polymers: PEDOT, **1**; PProDOT, **2**; and PProDOT-Me<sub>2</sub>, **3**.<sup>23</sup> A tandem chronoabsorptometry/chronocoulometry experiment was developed to measure CE values at 95% of the optical density change. Monomers were potentiostatically electropolymerized at +1.2 V vs a Ag/Ag<sup>+</sup> reference electrode to specific thicknesses (150 nm, as determined by profilometry in order to maximize the optical contrast) and areas (for charge density values) onto ITO-coated glass slides using a standard three-electrode system. Immediately following polymerization, polymer films were rinsed and subsequently switched (in monomer-free electrolyte solution) between the doped and neutral states 10 times in order to equilibrate the polymer film redox chemistry. Upon equilibration, films were transferred to a monomer-free electrolyte solution and probed with chronoabsorptometry (used to monitor the polymer absorbance at  $\lambda_{\text{max}}$ ) and chronocoulometry as the potential was stepped from the fully reduced and absorbing state (-1.0 V vs Ag/Ag<sup>+</sup> for 5 s), to the fully oxidized and transmissive state (+1.0 V for 5 s), and finally back to the fully reduced state (-1.0 V for 5 s), as shown in Figure 1.

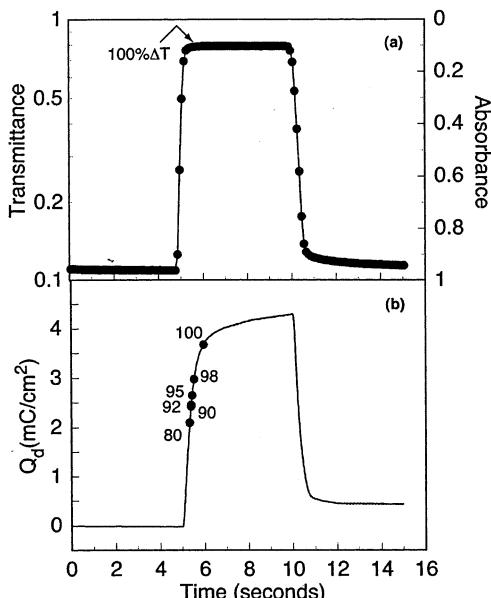
**Composite Coloration Efficiency Calculations.** The transmittance (%T) of the fully reduced films (%T<sub>red</sub>), which serve as baselines for the change in percent transmittance ( $\Delta\%T$ ) values, and the transmittance of the fully oxidized films (%T<sub>ox</sub>) were recorded, and the  $\Delta\%T$  values are given in Table 1. The difference between these two values is 100% of the full switch.  $\Delta\%T$  values ranging from 80 to 100% of the full electrochromic switch were determined by matching the time (t<sub>ox</sub>) required to achieve the desired percentage of switching (Figure 1a) to the corresponding charge density (Q<sub>d</sub>) in the chronocoulometry experiment, as shown in Figure 1b.  $\Delta\text{OD}$  was determined, and the CE values were then calculated at each of the  $\Delta\%T$  values by utilizing eq 1. Alternatively, the change in optical density (absorbance) can be monitored as a function of

(23) (a) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183. (b) Chung, T.-C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702. (c) Apperloo, J. J.; Janssen, R. A. J. *Synth. Met.* **1999**, *101*, 373. (d) Bäuerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217. (e) Fesser, K.; Bishop, A. R.; Campbell, D. K. *Phys. Rev. B* **1983**, *27*, 4804. (f) Cornil, J.; Beljonne, D.; Brédas, J. L. *J. Chem. Phys.* **1995**, *103*, 834. (g) Rughooputh, S. S. V.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1071. (h) Furukawa, Y. *J. Phys. Chem.* **1996**, *100*, 15644. (i) Doblhofer, K.; Rajeshwar, K. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; pp 531–588. (j) Apperloo, J. J.; van Haare, J. A. E. H.; Janssen, R. A. J. *Synth. Met.* **1999**, *101*, 417. (k) Aasmundtveit, K. E.; Samuelsen, E. J.; Inganäs, O.; Pettersson, L. A. A.; Johansson, T.; Ferrer, S. *Synth. Met.* **2000**, *113*, 93.

**Table 1. Optical and Electrochemical Data Collected for Coloration Efficiency Measurements**

conditions	% of full switch	$\Delta\%T^b$	$t_{ox}$ (s)	$Q_d^b$ (mC/cm <sup>2</sup> )	$\Delta\text{OD}^{b,c}$	CE (cm <sup>2</sup> /C)	doping level ( $R^d$ )
PEDOT							
$\lambda_{\text{max}} = 585 \text{ nm}$	80	43	0.27	2.13	0.44	206	0.15
$27.94 \text{ mC/cm}^2 = Q_p$	90	48	0.31	2.41	0.47	195	0.17
electrode area = 1.4 cm <sup>2</sup>	92	49	0.33	2.49	0.48	192	0.18
% $T_{\text{red}} = 24.77\%$	95	51	0.36	2.68	0.49	183	0.19
% $T_{\text{ox}} = 78.50\%$	98	53	0.45	3.04	0.50	165	0.22
$\Delta\%T = 54\%$	100	54	0.75	3.64	0.50	137	0.26
PProDOT							
$\lambda_{\text{max}} = 578 \text{ nm}$	80	53	0.32	2.04	0.69	340	0.17
$23.69 \text{ mC/cm}^2 = Q_p$	90	59	0.37	2.39	0.73	305	0.20
electrode area = 1.4 cm <sup>2</sup>	92	61	0.39	2.44	0.74	303	0.21
% $T_{\text{red}} = 13.41\%$	95	63	0.43	2.63	0.75	285	0.22
% $T_{\text{ox}} = 79.20\%$	98	65	0.50	2.97	0.76	255	0.25
$\Delta\%T = 66\%$	100	66	0.95	3.75	0.77	205	0.32
PProDOT-Me <sub>2</sub>							
$\lambda_{\text{max}} = 585 \text{ nm}$	80	61	0.23	1.75	0.75	428	0.18
$18.99 \text{ mC/cm}^2 = Q_p$	90	68	0.29	1.89	0.79	417	0.20
electrode area = 1.4 cm <sup>2</sup>	92	70	0.30	1.95	0.80	410	0.21
% $T_{\text{red}} = 13.05\%$	95	72	0.35	2.19	0.82	375	0.23
% $T_{\text{ox}} = 89.12\%$	98	75	0.39	2.36	0.83	352	0.25
$\Delta\%T = 76\%$	100	76	0.78	3.00	0.83	277	0.32

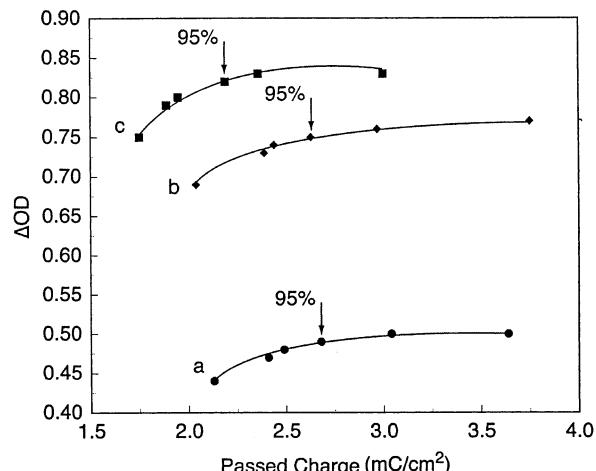
<sup>a</sup> Film thickness = 150 nm for all polymers. <sup>b</sup>  $\Delta\%T = \%T_{\text{ox}} - \%T_{\text{red}}$ ; values are an average of three different films. <sup>c</sup>  $\Delta\text{OD} = \log[T_{\text{ox}}/T_{\text{red}}]$ . <sup>d</sup> Doping levels calculated as follows:  $R = 2Q_{\text{ox}}/Q_p$  where  $Q_{\text{ox}}$  is the charge passed during doping and  $Q_p$  is the charge passed during polymerization.



**Figure 1.** Tandem (a) chronoabsorptometry/(b) chronocoulometry experiment for PProDOT depicting where 80, 90, 92, 95, 98, and 100% of the full contrast occurs upon polymer oxidation from -1.0 to +1.0 V and back to -1.0 V vs Ag/Ag<sup>+</sup>.

time and CE values can be calculated. Figure 1a displays both the transmittance and optical density change as a function of time while the polymer is switched between the absorbing, neutral state and the transmissive, oxidized state.

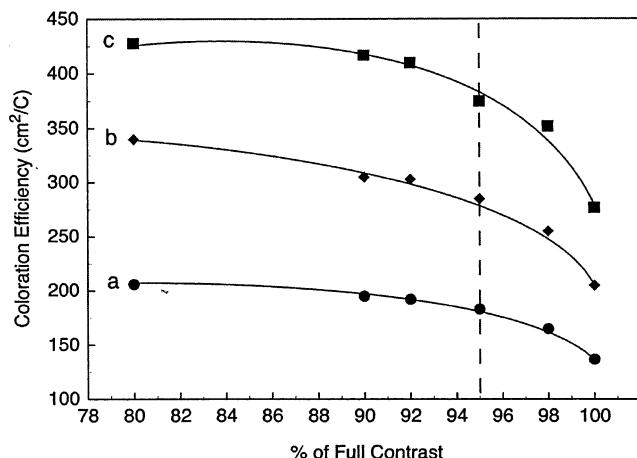
As can be seen from the tandem experiment, 80% of the full switch (completely neutral to completely doped/oxidized) is reached quickly (~0.3 s) and corresponds to about one-half of the total charge uptake of the polymer film. More importantly, 100% of the full optical change does not correlate with the maximum of the charge accumulation results (Figure 1b). This emphasizes the fact that it is imperative to measure the passed charge at very specific transmittance/absorbance values and not to simply record the maximum charge passed,



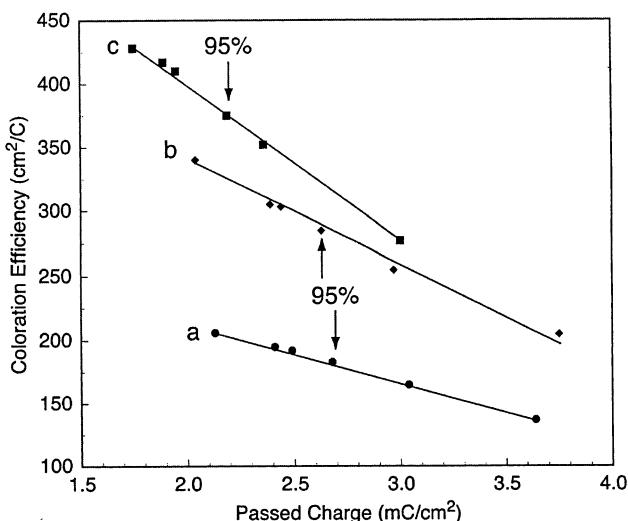
**Figure 2.** Optical density ( $\Delta\text{OD} = \log[T_b/T_c]$ ) of (a) PEDOT (●), (b) PProDOT (◆), and (c) PProDOT-Me<sub>2</sub> (■) as a function of vs the passed charge ( $Q_d$ ) at specific  $\Delta\%T$  values (80, 90, 92, 95, 98, and 100%).

since this value increases indefinitely due to background currents, as well as the capacitive nature of the conducting polymer films. The background currents attributed to supporting electrolyte side reactions were subtracted by repeating the experiment with a blank ITO slide, thus yielding a more accurate picture of the charge being passed solely through the polymer film.

To provide a point of reference with which to compare the CE values of various EC materials, the charge passed at 95% of the full optical switch will be used for reporting the composite CE measurements. We have selected this point since the majority of the color change has taken place and the last 5% is difficult to perceive with the naked eye. This is evident in Figure 2, which shows the change in optical density ( $\Delta\text{OD}$ ) as a function of the charge passed ( $Q_d$ ) during the switch. This same trend is observed in  $\text{M}_x\text{WO}_3$  films whereby a saturation of states (in this case from  $\text{W}^{6+}$  to  $\text{W}^{5+}$ ) has been achieved.



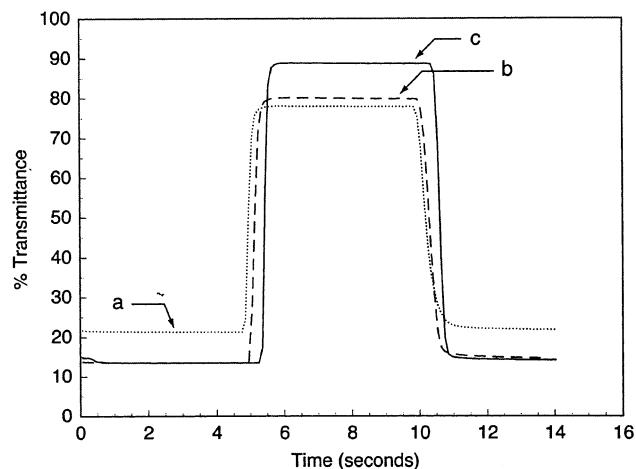
**Figure 3.** Coloration efficiency plotted vs % of the full contrast for 150 nm thick films of (a) PEDOT (●), (b) PProDOT (◆), and (c) PProDOT-Me₂ (■). Values are an average of three films. The dashed line indicates 95% of the full switch.



**Figure 4.** Coloration efficiency plotted vs the passed charge ( $Q_d$ ) for (a) PEDOT (●), (b) PProDOT (◆), and (c) PProDOT-Me₂ (■).

PProDOT-Me₂ displays the highest coloration efficiency ( $375 \text{ cm}^2/\text{C}$ ) when compared to its analogues PEDOT ( $183 \text{ cm}^2/\text{C}$ ) and PProDOT ( $285 \text{ cm}^2/\text{C}$ ) at 95% of the full switch, as shown in Figure 3. PProDOT-Me₂ requires smaller amounts of passed charge to achieve the switch and has higher  $\Delta\text{OD}$  values than PEDOT or PProDOT, suggesting that polymer structure is a major contributor to EC properties. Beyond 95% of the full switch, the coloration efficiency decreases as a function of the percent of full contrast, due to larger amounts of charge being injected into the film to reach 100%  $\Delta T$  without corresponding changes in optical density. Up to and until that point, the CE is relatively stable.

Examination of the composite CE as a function of passed charge in Figure 4 shows a continuous and linear decrease. This decrease is likely due to a lower true efficiency of creating a color change as the polymer's oxidation state saturates at an equilibrium value for the potential applied. The relationship between injected charge and corresponding color change is also exemplified here in that PProDOT-Me₂ requires smaller amounts

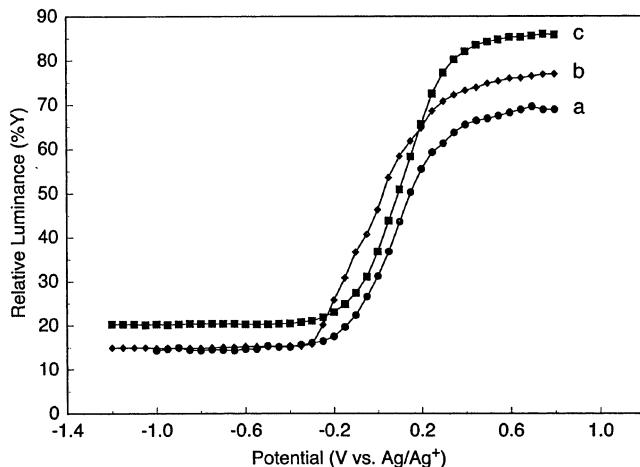


**Figure 5.** Chronoabsorptometry experiments for 150 nm thick films of (a) PEDOT (···), (b) PProDOT (— — —), and (c) PProDOT-Me₂ (—), where the films were switched from the fully neutral state ( $-1.0 \text{ V}$ ) to the fully oxidized state ( $+1.0 \text{ V}$ ) and back to the neutral state ( $-1.0 \text{ V}$ ) vs  $\text{Ag}/\text{Ag}^+$ .

of charge to achieve high amounts of contrast compared to its analogous family members. Decreased charge requirements for corresponding large optical modulation is desired for EC materials. At 95% of the full switch,  $2.19 \text{ mC/cm}^2$  is passed in the case of PProDOT-Me₂, while PEDOT requires  $2.68 \text{ mC/cm}^2$  and PProDOT requires  $2.63 \text{ mC/cm}^2$ .

Coloration efficiency is also directly related to the contrast ratios in conducting organic polymers, as well as injected charge. This is evident by comparing the chronoabsorptometry experiments for each of the polymers studied, as shown in Figure 5. All three polymers have rapid onsets of color change from the neutral state to the fully oxidized state. However, PProDOT-Me₂ has the highest contrast ratio, exhibiting a  $\Delta\%T$  of 76%, compared to 66% for PProDOT and 54% for PEDOT for 150 nm thick films. In addition, it is noteworthy to mention that PProDOT-Me₂'s enhanced electrochromism is not limited to single wavelengths, but rather is expressed across the entire visible region through luminance experiments.

**In Situ Colorimetry.** Relative luminance ( $\Delta\%Y$ ) studies, which measure the amount of light transmitted through the polymer film (its lightness or darkness), were performed on 150 and 300 nm thick films of the PXDOTs using the methodology previously reported by our research group.<sup>14a</sup> These experiments reveal that PProDOT-Me₂ possesses a higher contrast ratio across the visible region ( $\sim 450\text{--}750 \text{ nm}$ ), having a  $\Delta\%Y$  of 65% in 150 nm thick films, as shown in Figure 6 and summarized in Table 2. In fact, even as the thickness of the film is doubled, Figure 7 shows that PProDOT-Me₂ maintains the high  $\Delta\%Y$  (67%) while the other two polymers'  $\Delta\%Y$  begin to decrease. As the thickness is increased to 300 nm, PProDOT-Me₂ becomes less luminant in the reduced state while the high luminance is maintained in the oxidized state. This is due to the repression of the NIR absorbance tailing into the visible region in PProDOT-Me₂. Also, there is a shift in the onset of oxidation potential from the 150 nm films to the 300 nm films. An increased conjugation length associated with longer polymerization times and thicker films are plausible explanations.

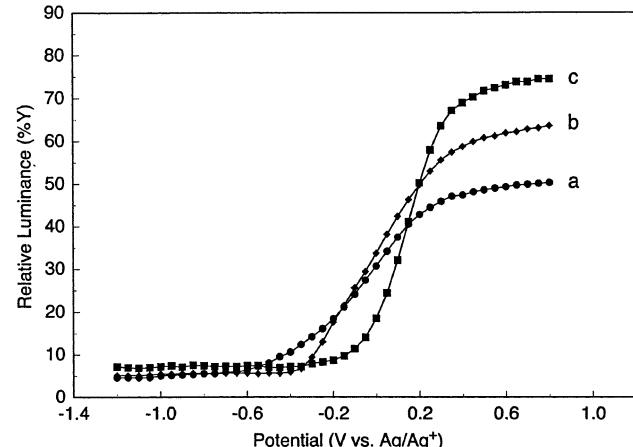


**Figure 6.** Relative luminance (% Y) vs applied potential (V vs  $\text{Ag}/\text{Ag}^+$ ) for 150 nm thick films of (a) PEDOT (●), (b) PProDOT (◆), and (c) PProDOT-Me<sub>2</sub> (■) polymerized potentiostatically at +1.2 V vs  $\text{Ag}/\text{Ag}^+$ . For each polymer, the potential was stepped in 50 mV increments from the fully neutral state (-1.2 V) to the fully doped state (+0.8 V).

**Table 2. Percent Transmittance, Percent Luminance, and Values for the PXDOTs**

polymer	$\Delta\% T^{a,b,d}$ (%)	$\Delta\% Y^{b,d}$ (%)	$\Delta\% Y^{c,d}$ (%)
PEDOT	54	55.8	45.6
PProDOT	66	61.9	58.4
PProDOT-Me <sub>2</sub>	76	65.5	67.3

<sup>a</sup> Values measured at each polymer's maximum absorption. <sup>b</sup> 150 nm thick films. <sup>c</sup> 300 nm thick films. <sup>d</sup> Values are an average of three films for each polymer.



**Figure 7.** Relative luminance (% Y) vs applied potential (V vs  $\text{Ag}/\text{Ag}^+$ ) for 300 nm thick films of (a) PEDOT (●), (b) PProDOT (◆), and (c) PProDOT-Me<sub>2</sub> (■) polymerized potentiostatically at +1.2 V vs  $\text{Ag}/\text{Ag}^+$ . For each polymer, the potential was stepped in 50 mV increments from the fully neutral state (-1.2 V) to the fully doped state (+0.8 V).

These observations hint to higher doping levels being the reason for increased contrast ratios (by shifting the carrier bands of the bipolarons out into the NIR). Thicker films would require more charge-compensating counterions to complete the oxidation. PProDOT-Me<sub>2</sub>, with its more sterically bulky structure, is able to incorporate more of these ions more effectively, thus resulting in higher contrast ratios, even in thick films. Doping levels until now have not been determined for a homologous series of PXDOTs for comparison purposes. Doping levels ( $R$ ) for the three polymers studied

were calculated on the basis of the charges required for polymerization ( $Q_p$ ) and doping ( $Q_{ox}$ ) of the film, as shown in eq 2.<sup>24</sup>

$$R = 2Q_{ox}/Q_p \quad (2)$$

The factor of 2 is derived from the generally accepted mechanism for oxidative electropolymerization where two electrons are transferred for each monomer unit incorporated into the polymer chain.<sup>25</sup> PEDOT, PProDOT, and PProDOT-Me<sub>2</sub> were found to have doping levels of 0.19, 0.22, and 0.23 at 95% of the full switch, respectively, or about one charge per four to five repeat units. An examination of the crystal structure of ProDOT-Me<sub>2</sub> shows that the alkylenedioxy bridge is not coplanar with the rest of the thiophene heterocycle, in contrast to EDOT.<sup>7</sup> Also, the dimethyl substitution is orthogonal to the rest of the fused ring system. These structural features allow for more accessible volume in the polymer film in which dopant ions can be incorporated. The open nature of the film makes it possible for counterions to move more freely in and out of the polymer film as opposed to PEDOT, which is more planar. PProDOT-Me<sub>2</sub> is therefore able to reach higher doping levels than PEDOT or PProDOT, which allows suppression in the intensity of the intermediate polaron peak location at the boundary between the visible and NIR regions.<sup>7</sup> This leads to higher contrast ratios and ultimately higher coloration efficiencies.

The variations in CE may also have spectroscopic implications. Examination of the spectroelectrochemical series of the PXDOTs reveals that the neutral absorbance for PEDOT is more broad and less structured than those of PProDOT and PProDOT-Me<sub>2</sub>.<sup>5,7</sup> Also, for films of similar thickness, PProDOT-Me<sub>2</sub> is more highly absorbing than PProDOT and PEDOT, meaning that it will have more optical density to deplete during switching. Also, the near-infrared absorbance peak that tails into the visible region for the oxidized spectrum of PProDOT-Me<sub>2</sub> is suppressed more than PEDOT's or PProDOT's, leading to increased coloration efficiencies.

## Conclusions

To quantitatively compare the electrochromism of organic polymers to each other and to classically studied inorganic materials ( $\text{WO}_x$ ,  $\text{IrO}_2$ ), a general method for measuring the efficiency of color change with respect to structure was developed. A family of poly(3,4-alkylenedioxythiophenes) was employed to measure their *composite* coloration efficiency and to understand more fully the reasons why different polymers possess varying coloration efficiencies. A tandem chronoabsorptometry/chronocoulometry experiment was utilized that accurately and reproducibly monitored the *composite* coloration efficiency of electrochromic materials. Factors such as structure and doping levels play a significant role in the ultimate electrochromic properties of the polymer. PProDOT-Me<sub>2</sub> demonstrated the highest coloration efficiency compared to PEDOT and PProDOT, as well as more widely studied inorganic electrochromic

(24) Reynolds, J. R.; Child, A. J.D.; Ruiz, J. P.; Hong, S. Y.; Marynick, D. S. *Macromolecules* **1993**, *26*, 2095.

(25) Baker, C. K.; Reynolds, J. R. *Electroanal. Chem.* **1988**, *251*, 307.

oxides and organic polymers. Such higher values may be attributed to spectral characteristics and increased doping levels, which reveal themselves not only at the polymers' maximum absorption ( $\lambda_{\text{max}}$ ) but over the entire visible region, making the PXdOTs attractive electrochromic materials for device applications. In the future, we will direct work toward more traditional slow CE measurements to further probe the coloration efficiency in the PXdOT family of electrochromic polymers. Further, we will utilize overall luminance changes that integrate over the entire visible spectrum while taking the sensitivity of the human eye into account.

## Experimental Section

**Chemicals.** Acetonitrile (ACN) was purchased from Fisher and distilled from  $\text{CaH}_2$ . Tetrabutylammonium perchlorate (TBAP) was synthesized by the metathesis reaction of perchloric acid (70% in water) and tetrabutylammonium bromide dissolved in water. The white crystals were washed with diethyl ether, recrystallized from ethanol, and dried under vacuum. The monomers were obtained as follows: EDOT was purchased from Aldrich and was purified by vacuum distillation (65 °C at 0.2 mmHg) prior to use; ProDOT<sup>7</sup> and ProDOT-Me<sub>2</sub>7 were prepared according to methodologies previously reported.

**Instrumentation.** The potentials were controlled and the polymers were characterized by use of an EG&G Princeton Applied Research model 273 potentiostat/galvanostat under the control of Scribner and Associates' Corrware II software. Chronoabsorptometry experiments were carried out using a Varian Cary 500 Scan UV-vis-NIR spectrophotometer. Luminance measurements were obtained by the use of a Minolta CS-100 Chroma Meter and CIE recommended normal/normal (0/0) illuminating/viewing geometry for transmittance measurements.<sup>26</sup> The sample was illuminated from behind by a D50 (5000 K) light source in a light booth specifically designed to exclude external light. A background measurement was

taken using a blank ITO slide in an electrolyte solution held in a standard quartz cuvette. The  $Y_{xy}$  values of the standard illuminant were measured and converted to the  $X_n$ ,  $Y_n$ ,  $Z_n$  tristimulus values of the standard illuminant.<sup>27</sup>

**Polymer Deposition and Characterization.** Electrochemical polymerizations were carried out using 10 mM monomer/0.1 M TBAP/ACN solutions. Prior to polymerization, the solutions were bubbled with an argon purge to remove any trapped oxygen. ITO-coated glass slides (7 × 50 × 0.6 mm, 20 Ω per square) were purchased from Delta Technologies. ITO slides were pretreated by first washing them in a 1 M HCl solution followed by a rinse with deionized water in order to remove any trace of adhesive/impurities on the surface. All polymers were electrodeposited onto the conducting ITO substrate under potentiostatic conditions (+1.2 V), using a three-electrode system (stainless steel counter electrode, Ag/Ag<sup>+</sup> reference electrode, and an ITO-coated glass slide working electrode), for specified time periods to ensure the proper thickness for maximum contrast (150 nm). (Several films were deposited for each polymer passing various amounts of charge. The films were then analyzed by spectroelectrochemistry, to assess the contrast of the films, and profilometry, to construct a calibration curve correlating charge density to film thickness.) Once the polymer had been deposited, the slide was immediately wiped off and more polymer was electrodeposited onto the same slide. We have observed that repeated polymerizations/wipings yield smooth, defect-free films, suitable for colorimetry and UV-vis experiments. Polymer films were then cycled 10 times in monomer-free electrolyte solution for equilibration purposes.

**Acknowledgment.** We acknowledge funding of this work from the Army Research Office (MURI program # DAAD19-99-1-0316 and EIC grant #DACA39-99-C-0004) and the Air Force Office of Scientific Research (F49620-00-1-0047).

CM020433W

(26) Marcus, R. T. In *Color for Science, Art, and Technology*; Nassau, K., Ed.; Elsevier: Amsterdam, 1998; pp 31–96.

(27) Wuszecki, G.; Stiles, W. S. *Color Science*; Wiley: New York, 1982.