Electrochemical Copolymerization and Spectroelectrochemical Characterization of 3,4-Ethylenedioxythiophene and 3,4-Ethylenedioxythiophene−Methanol Copolymers on Indium−Tin Oxide

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ABSTRACT: This work describes the electrochemical copolymerization and spectroelectrochemical characterization of 3,4-ethylenedioxythiophene (EDOT) with a commonly used EDOT derivative: 2,3-dihydrothieno[3,4-*b*]-1,4-dioxyn-2-yl methanol (EDTM), on indium−tin oxide (ITO) electrodes, as a function of the EDTM/EDOT comonomer feed ratio. The potential of initial polymerization and the degree of optical contrast between reduced and oxidized states increased steadily with increasing proportions of EDTM. Reactivity ratios were determined by spectroscopic characterization of the copolymer film and by monitoring the depletion of monomer from the starting solution by liquid chromatography, following the formation of relatively thick PEDOT/PEDTM films. Average reactivity ratios of 1.5 ± 0.2 and 0.4 ± 0.3 were obtained for EDOT and EDTM, respectively, demonstrating preferential deposition of EDOT on ITO electrode surfaces. Significant differences were noted at low and high degrees of conversion, indicating changes in copolymer composition with film thickness. These results have real significance for the characterization of electron-transfer rates for the first monolayer of PEDOT/PEDTM on ITO, determined by a new mode of potential-modulated attenuated total reflectance spectroelectrochemistry.[1]

Introduction

Conductive polymers synthesized from 3,4-alkylenedioxythiophene derivatives have become an important class of organic electronic materials due to their inherent stability, low oxidation potential, high conductivity, and excellent electrochromic properties.[2] The most highly studied derivative is poly(3,4-ethylenedioxythiophene), or PEDOT, produced by oxidative polymerization of its monomer unit, EDOT, shown in Figure 1. PEDOT and related materials have been used in applications ranging from amperometric biosensing[3−6] to molecular electronics,[7] and dispersions of PEDOT with polystyrenesulfonate (PEDOT:PSS) are now commonly used as modifying layers for ITO electrodes in the production of thin film photovoltaic cells[8] and organic light-emitting diodes (OLEDs).[9−11] The net effect of the PEDOT:PSS layer in these systems is fourfold: (i) PEDOT:PSS films help to planarize the ITO surface, (ii) PEDOT:PSS films appear to make the ITO surface more uniformly electroactive, (iii) the PEDOT:PSS layer reduces the electrode surface polarity, making it more compatible with nonpolar components of OLEDs and OPVs, and (iv) the PEDOT:PSS layer appears to increase the effective work function of the resulting substrate.[8]

In their neutral state, PEDOT and PEDOT derivatives absorb strongly across the visible wavelength region, creating a deeply colored material. When oxidatively doped, the absorbance shifts into the near-IR region, yielding nearly transparent thin films. This electrochromic effect has been noted for polymers created from a wide variety of monomers in a series of publications by Kumar et al.[12,13] and Reynolds and co-workers.[14−20] These studies have shown that the presence of substituent groups on the polymer backbone, or increasing the size of the alkylenedioxy bridge, significantly enhances the optical contrast between the neutral and doped states by inducing an increased torsional twist in the conjugated system. Furthermore, these structural changes significantly alter the band-gap energy of the polymer, producing significant shifts in the wavelength region over which the electrochromic effect takes place. This phenomenon is not limited to polymerizations involving a single monomer (homopolymerization) but is also seen in conductive polymer blends, copolymers, and laminate structures, allowing one to specifically tailor the electrochromic switching to the wavelength region of interest.[21]

Substitution of side groups onto the polymer backbone not only changes the optical properties of the material but can also be used to introduce functional groups. Polymerization of EDOT−methanol (2,3-dihydrothieno[3,4-*b*]-1,4-dioxyn-2-yl methanol), or EDTM,[22−25] shown in Figure 1, is a common strategy to create a PEDOT-like material bearing hydroxyl groups which are a convenient point of attachment for a variety of functional groups, including cyanobiphenyl,[13] tetrathiafulvalene,[24] and poly(ethylene glycol) (PEG) chains and linker arms.[23−25] The electropolymerization and spectroelectrochemical properties of PEDTM homopolymer have been briefly characterized relative to PEDOT[22,23] and display a redox behavior defined by narrower voltammetric peak widths and decreased peak separation. The optical absorption maximum ($\lambda_{\max}$) of neutral PEDTM is slightly red-shifted at 596 nm, compared to 580 nm obtained for PEDOT.[23]

Copolymerization of EDOT with other monomers provides a means of creating new conductive polymeric systems and electrode coatings[26−28] with functionalized components,[29] tunable optical properties,[30−32] and adjustable doping levels.[33] For example, *N*-alkylcarbazole derivatives have been copolymerized with EDOT both chemically[30,31] and electrochemically[28,32] to create materials in which the optical band gap depends on the

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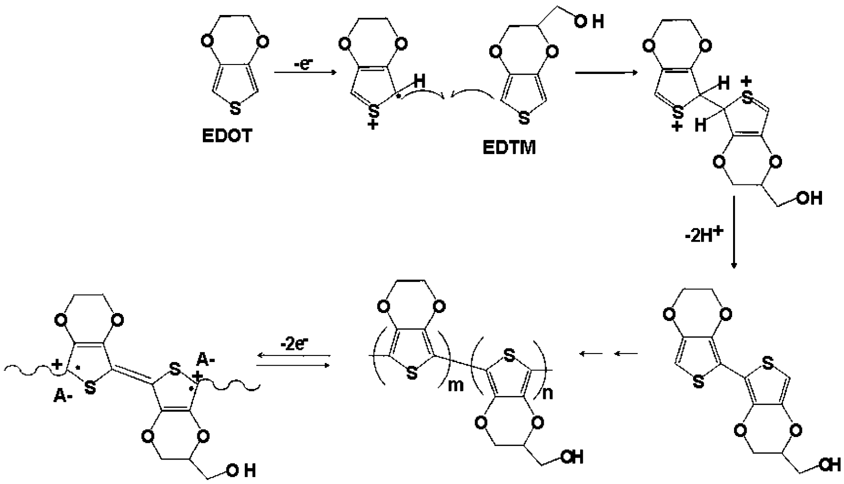

Figure 1. Electrocopolymerization of EDOT with EDTM. The initial oxidation of monomer takes place at the ITO electrode. The polymerization proceeds through a radical chain mechanism, incorporating both monomers into the growing polymer. Further oxidation of the polymer (lower left) produces a conductive bipolaron state.

molar ratio of monomer constituents. Simultaneous electrodeposition of EDOT with thieno[3,4-*b*]thiophene yielded a copolymer with significantly enhanced stability to cathodic doping.[33] Polymer structures containing EDTM can be covalently modified before or after polymerization. Roncali et al.[29] have shown that ferrocene-modified EDTM can be covalently incorporated into PEDTM, or oligo(PEG)-modified PEDTM, to produce a functionalized polymeric electrode surface.

For the design of specific copolymeric systems and control of the degree of functionalization, it is important to be able to predict the copolymer composition, i.e., the relative proportions of each monomer constituent. This requires accurate knowledge of the relative reactivity of the two monomers toward a radical species and, in the case of electropolymerization, reactivity toward the electrode surface. While many of the aforementioned studies regarding the copolymerization of EDOT report a preferential reactivity of one monomer vs the other,[27,30−32] they do not present a quantitative assessment of relative monomer reactivity during electropolymerization. This work details the spectroelectrochemical properties of conductive polymer films produced via electrocopolymerization of EDOT with EDTM. Reactivity ratios and copolymer composition are determined spectroelectrochemically and by bulk monomer depletion studies. A companion work, published elsewhere,[1] details the spectroelectrochemical characterization of PEDOT/PEDTM copolymer films on ITO substrates using potential-modulated spectroelectrochemical attenuated total internal reflectance (ATR), wherein we show that the electrochromic switching rate of these films is significantly lowered with increasing fraction of EDTM incorporated into the copolymer film, owing to the interaction of the pendant methanol groups with the ITO surface.

Experimental Section

Materials. Unless otherwise stated, all chemicals were supplied by Aldrich and used without further purification. 3,4-Ethylenedioxythiophene−methanol (EDTM) was synthesized in the Organic Synthesis Facility at the University of Arizona according to procedures outlined by Lima[22] and Akoudad.[23] Monomer solutions (both EDOT and EDTM) were made in 0.1 M $LiClO_4$(aq) with 10% v/v methanol by predissolving the monomer in the methanol fraction.

Indium−tin oxide (ITO)-coated glass substrates were obtained from Colorado Concept Coatings, with a resistivity of ∼16 Ω/square and root-mean-square surface roughness of 2.5 nm. Substrates were cleaned by first light scrubbing with Alconox cleaner and a cotton pad and then rinsing with deionized water (18.0 MΩ Barnstead/Thermolyne Nanopure). Substrates were then blown dry with nitrogen and cleaned in an air plasma (Harrick PDC-3XG) for 5 min at 15 W.

Spectroelectrochemical Measurements. All electrochemistry was performed using a EG&G model 263A potentiostat. The electrode cell consisted of a platinum wire (Aldrich 99.99+%) counter electrode, a commercial Ag/AgCl reference electrode (Bioanalytical Systems), and an ITO-coated glass substrate as the working electrode. Electrical contact to the ITO was made via a brass foil contact. All potentials stated in this work are vs Ag/AgCl. Spectroelectrochemical data were obtained using a single-pass transmission cell designed to mount onto the sample platform of a Spectral Instruments series 400 fiber-optic spectrophotometer. Spectra were acquired at 100 mV intervals while simultaneously sweeping the potential of the ITO electrode at 25 mV/s.

Determination of Reactivity Ratios. A thorough review of reactivity ratios, and the various methods used in their determination, has been described by Odian[35] and will be briefly discussed here. Reactivity ratios (r) for a two-monomer system are defined according to the following expressions for the four possible monomer−monomer reactions

$$
\begin{aligned}
M_1^{\bullet} + M_1 &\xrightarrow{k_{11}} M_1M_1^{\bullet} \\
M_1^{\bullet} + M_2 &\xrightarrow{k_{12}} M_1M_2^{\bullet} \\
M_2^{\bullet} + M_1 &\xrightarrow{k_{21}} M_2M_1^{\bullet} \\
M_2^{\bullet} + M_2 &\xrightarrow{k_{22}} M_2M_2^{\bullet}
\end{aligned}
\tag{1}
$$

where M_1 and M_2 represent the two dissolved monomers and k is the rate coefficient for the reaction. From these expressions, the reactivity ratios are defined as

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \tag{2}$$

When $r > 1$, the monomer reacts preferentially with itself, and when $r < 1$, the monomer reacts preferentially with the second monomer. When $r = 1$, there is no preference. A “copolymer equation”[35] can be derived, using a steady-state assumption, to approximate the relative monomer composition of the resulting copolymer based on the initial concentrations of each monomer and the reactivity ratios

$$\frac{dM_1}{dM_2} = \frac{[M_1]}{[M_2]}\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \approx \frac{m_1}{m_2} \tag{3}$$

where dM is the change in monomer concentration as a result of polymerization, $[M_1]$ and $[M_2]$ are the initial monomer concentrations, and m_1/m_2 is the ratio of monomer units M_1 and M_2 in the resulting polymer. It is important to note that this equation does not account for the decrease in monomer concentrations during the course of polymerization and thus is only valid in the limit of low conversion (<5%).[35]

For higher degrees of conversion, an integrated form of eq 3 can be utilized[36−38]

$$D = 1 - \left[\frac{f_1}{(f_1)_0}\right]^{\alpha}\left[\frac{f_2}{(f_2)_0}\right]^{\beta}\left[\frac{(f_1)_0 - \delta}{f_1 - \delta}\right]^{\gamma} \tag{4}$$

where D is the degree of conversion and f_1 and f_2 are the mole fractions of M_1 and M_2, respectively. The zero subscripts denote initial conditions, and

$$\alpha = \frac{r_2}{1 - r_2} \quad \beta = \frac{r_1}{1 - r_1}$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \quad \delta = \frac{1 - r_2}{2 - r_1 - r_2}$$

In this study, monomer reactivity ratios in copolymer films of EDOT and EDTM electropolymerized on ITO were determined using two methods: (a) transmission UV−vis spectroelectrochemistry of the copolymer film and (b) by measuring the depletion of dissolved monomer from the comonomer feed solution. In the spectroelectrochemical method, expressions derived by Ramelow et al.[39] were used to extract reactivity ratios using the difference in molar absorptivity between the two homopolymers according to the expression

$$F_1 = \frac{m_1}{m_1 + m_2} = \frac{\epsilon_{12} - \epsilon_2}{\epsilon_1 - \epsilon_2} \tag{5a}$$

where F_1 is the mole fraction of monomer M_1 in the polymer and ϵ_1, ϵ_2, and ϵ_{12} are the molar absorptivities of homopolymer M_1, homopolymer M_2, and the copolymer, respectively. Equation 5a can be written in terms of the molar ratio of monomers by

$$\frac{\epsilon_{12} - \epsilon_2}{\epsilon_1 - \epsilon_{12}} = \frac{m_1}{m_2} \tag{5b}$$

Molar absorptivity values were obtained from the film absorbance as a function of polymer surface coverage, estimated from the integrated charge passed during electropolymerization, assuming 2.3 electrons per monomer.[40] Reactivity ratios were then obtained by calculating m_1/m_2 according to eq 5 and substituting into eq 3.

It is important to note that in this method the bulk properties of the copolymer film are measured, and a linear relationship between the molar absorptivity of the film and the degree of copolymerization is assumed. It is important that the comonomer feed ratio remain relatively constant during the film growth, such that one monomer is not significantly depleted from solution with respect the other. Thus, a relatively high concentration of monomer (10 mM) was used to prepare films of sufficient thickness for acceptable signal-to-noise in absorbance measurements, without significantly altering the concentrations of dissolved monomer, i.e., under conditions of low conversion. Polymerization was performed on ITO (electrode area of 0.5 cm^2) in an unstirred 2 mL volume cell via the application of a cyclic voltammetric potential waveform between −0.4 and 1.2 V at 25 mV/s.

Accurate determination of reactivity ratios via the second method, monomer depletion, requires (a) separation of monomer from polymer, which is a consequence of PEDOT/PEDTM electropolymerization in aqueous solution since the adsorbed polymer is insoluble, and (b) detection of relatively small changes in high concentrations of monomers, which is readily achieved using chromatography. Both EDOT and EDTM absorb strongly at 254 nm and can easily be separated by reverse-phase liquid chromatography (RPLC). A relatively small volume cell (3.5 mL) and large electrode (total area 12.9 cm^2) were utilized in order to obtain detectable decreases in monomer concentration. PEDOT/PEDTM films were grown by stepping the potential of the ITO electrode to 1.15 V in a stirred 1 mM solution of monomer for 15 or 30 s. Changes in monomer solution concentration were monitored before and after polymerization using a Thermo Separation Products HPLC with Spectra System P4000 gradient pumps, SN4000 and UV3000 detectors (254 nm), and a Spectra-Physics AS3000 autosampler. Separation was obtained using an Alltech Econosphere C-18 column with 5 μm particle size and a mobile phase of 50:50 acetonitrile: water with 0.1% trifluoroacetic acid. 3,3′-Bithiophene was used as an internal standard. At a flow rate of 1.25 mL/min, baseline-resolved peaks with approximate retention times of 1.9, 2.7, and 5.5 min were obtained for EDTM, EDOT, and 3,3′-bithiophene, respectively.

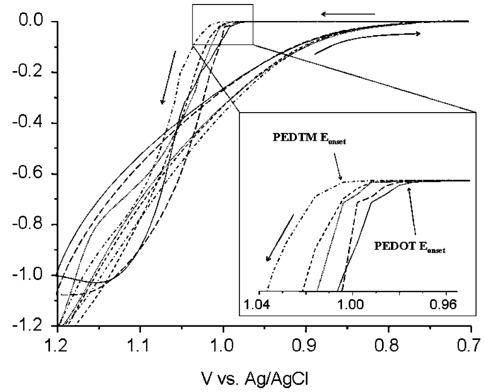

Figure 2. Electropolymerization of EDOT and EDTM monomers onto ITO. The arrows indicate sweep direction. During the initial voltammetric scan, the onset of polymerization is indicated by the precipitous increase in anodic current at ∼1.0 V. The onset of polymerization shifts to more positive values with increasing f_{EDTM} in the monomer solution (inset). $f_{EDTM} = 0$ (—), $f_{EDTM} = 0.25$ (− − −), $f_{EDTM} = 0.50$ (• • •), $f_{EDTM} = 0.75$ (- - -), and $f_{EDTM} = 1.0$ (• - •).

Results and Discussion

EDOT/EDTM Coelectropolymerization and Spectroelectrochemistry. A proposed mechanism for the copolymerization of EDOT and EDTM is shown in Figure 1, modeled after the electrochemical polymerization of pyrrole.[35] Polymerization is initiated at the electrode surface following the one-electron oxidation of monomer. Combination of the radical species with neutral monomer, followed by proton elimination, forms the neutral oligomer. The polymerization proceeds through subsequent oxidation of oligomer at the electrode to generate the radical species. The resulting polymer film can be repeatedly cycled between the insulating neutral form and the oxidized conductive bipolaron state.[41]

Cyclic voltammograms recorded during the electropolymerization of EDOT, EDTM, and comonomer solutions on bare ITO electrodes are shown in Figure 2. During the initial anodic sweep, no Faradaic current is apparent until ∼1 V, at which the current increases significantly, corresponding to the onset of monomer oxidation and subsequent electropolymerization. On the return sweep, polymerization continues at potentials positive of 0.80 V. This difference between the onset potential and the minimum potential required to sustain polymer growth creates a “nucleation loop”, characteristic of electropolymerization of conductive polymers.[42]

Table 1. Summary of Spectroelectrochemical Data for Thin Films of PEDOT/PEDTM Polymer and Copolymer Films as a Function of the Mole Fraction EDTM in Solution during Electropolymerization (f_{EDTM})

f_{EDTM}	E_{onset} (V)	λ_{max} (nm)	ϵ (cm^2/nmol)	contrast ratio at λ_{max}	$E°$ voltammetry (V)	ΔE_{peak} voltammetry (V)	E_{mid} absorpto-voltammetry (V)	ΔE_{peak} absorpto-voltammetry (V)
0	0.989	571	3.6	1.16	0.08	0.3	−0.24	0.05
0.25	0.997	577	4.3	1.45	0.1	0.2	−0.20	0.09
0.50	1.009	582	4.6	1.66	0.06	0.2	−0.18	0.05
0.75	1.008	583	5.5	1.77	0.06	0.2	−0.17	0.03
1	1.019	591	7.0	2.20	0.05	0.1	−0.17	0.01

Close examination of the initial voltammograms for EDOT, EDTM, and comonomer solutions (Figure 2, inset) reveals a significant increase in onset potential (E_{onset}) as the mole fraction of EDTM in solution (f_{EDTM}) is increased. The initial oxidation of EDTM occurs at potentials 0.030 V more positive than those for EDOT (see E_{onset} values listed in Table 1). In subsequent scans, continued growth of both PEDTM and PEDOT occurs at ~0.80 V and shows no significant dependence on the relative solution concentrations of monomer. This indicates that while the initial oxidation of EDOT at the ITO electrode is favored over that of EDTM, the degree of incorporation of both monomers onto existing polymer (i.e., after the first scan) is approximately equal.

Cyclic voltammograms of PEDOT/PEDTM copolymer films grown onto existing copolymer are shown as a function of increasing f_{EDTM} in Figure 3. The extremely broad voltammetric peaks are representative of a wide distribution of redox potentials and are somewhat difficult to discern from the non-Faradaic background; however, some assignments can be made. There is a small anodic voltammetric peak that increases in intensity and gradually shifts from +0.2 V in the 100% PEDOT film to +0.1 V in the 100% EDTM film, corresponding to the oxidative redox doping of the polymer. Also evident are a cathodic shoulder at −0.06 V and a peak at −0.2 V, corresponding to the reduction of the polymer film and subsequent counterion release, respectively,[22] that gradually shift, with increasing f_{EDTM}, to −0.2 and −0.3 V, respectively. The gradually increasing anodic current at ~0.8 V in all voltammograms represents the onset of electropolymerization from existing polymer and is independent of f_{EDTM}. Apparent values for the peak separation (ΔE_{peak}) and standard redox potential ($E°$) obtained from the voltammetric data are listed in Table 1. As f_{EDTM} increased, ΔE_{peak} decreased, whereas changes in $E°$ were relatively minor.

Transmission spectroelectrochemistry was used to examine the spectral properties of the polymer films as a function of both potential and monomer solution composition. Figure 4 shows absorbance spectra of the films after five scans in the oxidized (A) and the reduced (B) states as a function of f_{EDTM}.

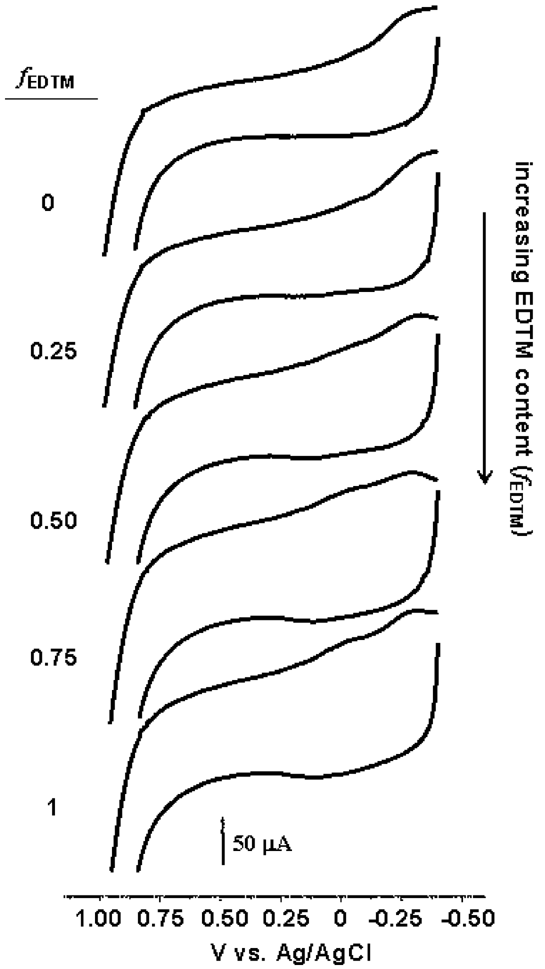

Figure 3. Cyclic voltammograms of PEDOT/PEDTM films on ITO, acquired at 25 mV/s, on the third voltammetric sweep from −0.40 to 1.20 V. Integration of the cumulative charge passed during the first three polymerizations, assuming 2.3 electrons per monomer unit, yields an estimated surface coverage of 95 nmol/cm^2. The arrow indicates the direction of increasing f_{EDTM} in solution, from 0 to 1 in 0.25 increments.

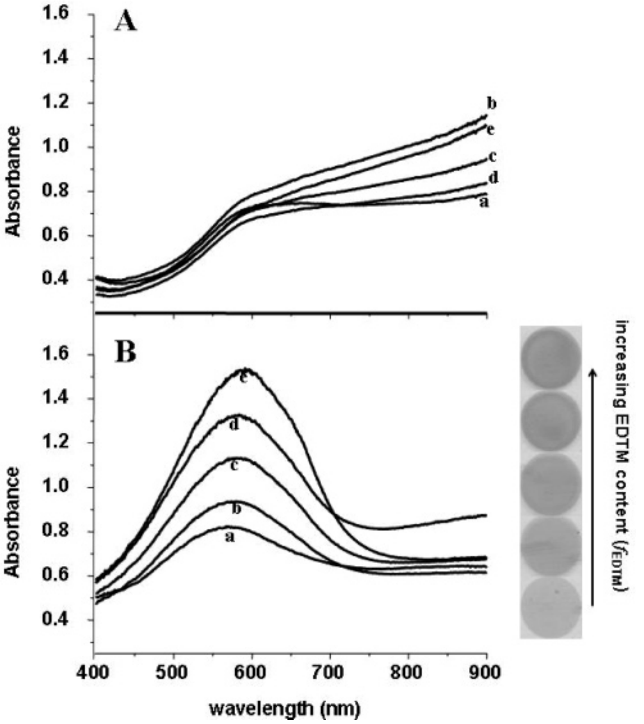

Figure 4. Transmission spectra of PEDOT/PEDTM copolymer films, after five voltammetric scans, held in the fully oxidized state at 0.50 V (A) and in the reduced state at −0.40 V (B). The arrows in (B) indicate a general trend of increasing molar absorptivity in the reduced state as a function of increasing EDTM mole fraction. f_{EDTM} = 0 (a), f_{EDTM} = 0.25 (b), f_{EDTM} = 0.50 (c), f_{EDTM} = 0.75 (d), and f_{EDTM} = 1.0 (e). To the right of (B) is a photographic series of reduced polymer films with increasing f_{EDTM} showing the substantial increase in molar absorptivity.

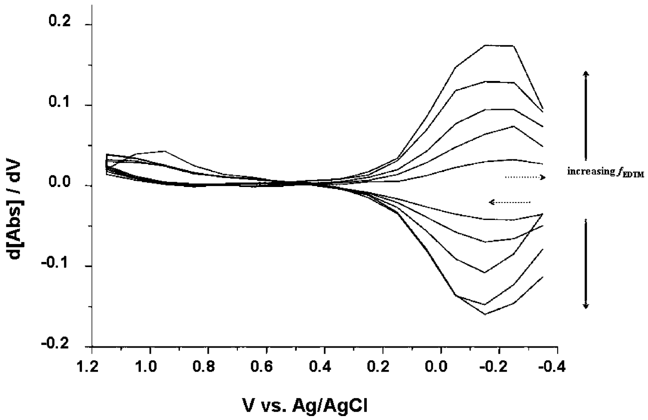

Figure 5. Absorptovoltammograms of PEDOT/PEDTM copolymer films obtained during the fourth scan and reconstructed from optical data as a function of potential. Solid arrows indicate the direction of increasing f_{EDTM} from 0 to 1 in increments of 0.25. The dotted arrows show the sweep direction.

The oxidized films show a gradual increase in absorbance with increasing wavelength and a general trend of increasing absorbance with f_{EDTM} at longer wavelengths. At wavelengths below 600 nm, however, the absorbance of the oxidized film is largely independent of f_{EDTM}. In contrast, the spectra of the reduced films (Figure 4B) display a clear absorbance shift in λ_{max}, from 571 nm for pure PEDOT to 591 nm for pure PEDTM (λ_{max} are listed in Table 1). This shift in wavelength has been attributed to an enhancement in the degree of conjugation, and a subsequent narrowing of the band-gap energy, due to the pendant hydroxymethyl substituent of EDTM.[23]

Most notably, the reduced state molar absorptivity (ϵ) of the films greatly increases with f_{EDTM}, as illustrated in the photographic series in Figure 4B. Listed in Table 1 are ϵ at λ_{max} for these polymers as well as the respective optical contrast ratios (defined as the ratio of the film absorbance in the reduced state to that in the oxidized state). The contrast ratio increases steadily with f_{EDTM}, from 1.16 for PEDOT to 2.20 for PEDTM, consistent with ϵ for PEDTM being nearly 2-fold greater than that of PEDOT. This trend has been seen in similar polymeric systems where the addition of substituent groups to the monomer unit substantially enhances the contrast ratio, or electrochromic effect, of the resulting polymer film.[14−16]

The high degree of electrochromism allows the extraction of electrochemical parameters via optical reconstruction of voltammetric data, i.e., absorptovoltammetry. Figure 5 shows a plot of the first derivative of the absorbance as a function of potential. In contrast to the conventional voltammetry shown in Figure 3, the electrooptical transitions in the absorptovoltammograms are clear due to the absence of non-Faradaic background. The major transition is centered about −0.2 V, extending to ~0.4 V. The anodic portion of this transition, during which film absorbance decreases, is represented by the lower half of the plot; in the upper, cathodic half of the plot, the absorbance increases. The magnitude of the absorbance change increases with f_{EDTM} for the copolymer blends and scales with the contrast ratio of the film. A second, minor transition is also evident in Figure 5 at potentials greater than 1 V. The increase in d[Abs]/dV in this region is due to greater film thickness as additional polymer is deposited on the electrode.

Apparent values for the peak separation (ΔE_{peak}) and standard redox potential ($E°$) obtained from the absorptovoltammetric data are listed in Table 1. The general trend is increasing $E°$ with increasing f_{EDTM}, and constant or slightly decreasing ΔE_{peak}, with discontinuities at the transitions from homopolymer to copolymer. Akoudad and Roncali[23] noted similar trends in $E°$ and ΔE_{peak} in voltammetry of PEDOT and PEDTM films on platinum microelectrodes and observed that the PEDTM redox transitions were more highly resolved and well-defined. A positive correlation between degree of monomer substitution and more positive $E°$ was also observed in previous studies,[43] including investigations of alkyl-substituted poly(3,4-propylenedioxypyrrole) derivatives,[18] and is likely due to the increased steric hindrance to conformational changes associated with the transfer of charge.

Table 2. Summary of Data for the Determination of Reactivity Ratios for EDOT and EDTM Electropolymerized onto ITO Electrodes

method of determination	r_1	r_2
film absorptivity (low conversion)[a]	1.31	0.31
solution depletion (low conversion)[a]	1.65	0.15
solution depletion (high conversion)[b]	1.58	0.71

[a] Low conversion refers to <5% depletion of available monomer from solution. Reactivity ratios calculated according to eq 3. [b] High conversion refers to ca. 50% depletion of available monomer from solution. Reactivity ratios calculated according to eq 4.

A comparison of the voltammetric and absorptovoltammetric data in Table 1 reveals significant differences between the electrochemical and electrooptical properties of the films. The absorptovoltammetric $E°$ values are significantly more negative than the corresponding voltammetric data. This shows that during an anodic voltammetric sweep the bulk of the change in absorbance has already occurred before the charge transfer is measured using conventional voltammetry. Thus, the electrooptical contrast is maximal before the film is fully oxidized; from a device perspective, this means that the film can be optically switched using a relatively lower applied voltage.

From a molecular perspective, this implies that the conformational changes that alter the optical properties within the visible wavelength regime occur at low doping levels, i.e., before the film is completely oxidized. While charge storage in electrochemically doped polythiophene films is largely in the form of bipolarons,[41,44] ESR studies have demonstrated a shift in the predominant charge carrier from polaron to bipolaron as the degree of doping is increased.[44] The results of the current study suggest that the most drastic conformational and optical changes are driven by the initial charge injection, and polaron formation, within the polymer film. At higher doping levels, the changes in optical properties are less pronounced as the bipolaron state becomes dominant and the film approaches a metallic state.[41]

Reactivity Ratios. Values for r_1 (EDOT) and r_2 (EDTM) obtained by both the monomer depletion and spectroelectrochemical methods are listed in Table 2. Regardless of method used or relative degree of conversion, they follow the same trend of $r_1 > 1$ and $r_2 < 1$. Furthermore, although spectroelectrochemistry is an indirect method (based on assuming a linear relationship between the change in molar absorptivity and degree of copolymerization), the r_1 and r_2 values obtained are comparable to those obtained using solution depletion. To compare EDOT and EDTM reactivity, we average the values obtained by all methods, yielding $r_1 = 1.5 \pm 0.2$ and $r_2 = 0.4 \pm 0.3$. The significant difference between these values demonstrates that EDOT is preferentially incorporated into the propagating copolymer. However, the values are sufficiently similar such that appreciable amounts of both monomers are incorporated over a large range of comonomer feed solutions. The relatively large relative error in the reactivity ratios is a result of the significant influence of the electrode surface and the dependence

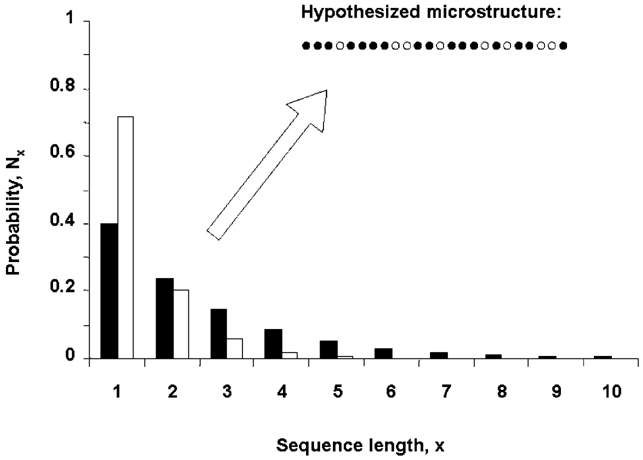

Figure 6. Sequence length distribution plot for electropolymerized PEDOT/PEDTM with equimolar feed solution of EDOT (●) and EDTM (○), calculated based on the treatment presented in ref 35. Reactivity ratios are 1.5 and 0.4 for EDOT and EDTM, respectively. The inset displays a hypothesized copolymer microstructure.

of the monomer reactivity on the surface coverage of the polymer film. These differences are discussed in greater detail below.

The inverse reactivity ratio, $1/r$, allows comparison of the relative reactivity of each monomer toward the propagating radical of the growing polymer.[35] This parameter is the ratio of the reaction rates of the radical with one monomer vs the other monomer, according to eq 2. For EDOT and EDTM, the $1/r_1$ and $1/r_2$ values are 0.67 and 2.5, respectively, indicating that for *both* monomers reaction with an EDOT radical is more rapid.

The microstructure of the copolymer, i.e., the arrangement of monomer units along the polymer backbone, can be qualitatively assessed by considering the product of the reactivity ratios, r_1r_2: (a) Values of $r_1r_2 > 1$ imply formation of a block copolymer. (b) When $r_1r_2 = 1$, the polymerization is ideal, yielding a statistically random assortment of monomer units along the polymer chain. (c) When r_1r_2 approaches 0, each monomer preferentially reacts with the other monomer, producing a chain with an alternating arrangement, e.g., $(M_1M_2)_n$. For EDOT/EDTM electropolymerization, $r_1r_2 = 0.6$, which, when considered along with the relatively large reactivity ratio for EDOT, again reflects some preference for EDOT incorporation.

Expressions relating the reactivity ratios and initial monomer concentrations to probable sequence length distributions have been summarized by Odian.[35] For a statistically random copolymer, the probability (N_x) of obtaining a specific sequence length (x) is equal for both monomers; thus, N_x would be 0.5 for both EDOT and EDTM at $x = 1$, and N_x would be 0.25 at $x = 2$, etc. For an alternating arrangement of monomer units (i.e., $M_1M_2M_1M_2$...), N_x would approach 1 at $x = 1$. A sequence length distribution plot for electropolymerized PEDOT/PEDTM, calculated assuming the mean reactivity ratios stated above and an equimolar comonomer feed solution, is shown in Figure 6. The plot shows that relatively longer sequence lengths are more probable for EDOT, whereas shorter sequence lengths are more probable for EDTM. This difference can be expressed by averaging across the probability distribution, which yields mean sequence lengths of 2.5 and 1.4 for EDOT and EDTM, respectively. A hypothesized microstructure that reflects these data is shown schematically in Figure 6 (inset).

Last, we contrast the reactivity ratios obtained by solution depletion at low and high conversion, which provides some insight regarding the influence of the ITO surface on copolymer composition and relative monomer reactivity. The low (<5%) and high (>50%) degrees of conversion (Table 2) correspond to approximately 4 and 80 equivalent monolayers of polymer, respectively, assuming a mean molecular area of 10 Å^2 per monomer. At low surface coverage, EDTM is considerably less reactive than at higher coverage ($r_{2,\mathrm{low}} = 0.15$; $r_{2,\mathrm{high}} = 0.71$). To illustrate this difference, the measured $r_{2,\mathrm{low}}$ and $r_{2,\mathrm{high}}$ values were applied to eq 3 at various initial comonomer feed concentrations ($[M_1]$ and $[M_2]$), yielding the plots of the resulting copolymer composition shown in parts A and B of Figure 7, respectively. The fraction of EDTM incorporated into the polymer (F_{EDTM}), for an equimolar comonomer feed solution, is ~0.30 at low conversion and 0.40 at high conversion. This difference is likely due to the lower E_{onset} for the initial deposition of EDOT on ITO (Table 1). At 1.15 V, the potential at which the polymer films were grown, there is a 30 mV higher overpotential for the electropolymerization of EDOT as compared to EDTM, resulting in the preferential deposition of EDOT. After a sufficiently thick polymer coating is formed (higher degree of conversion), E_{onset} equalizes for both monomers at ~0.80 V, and the proportion of EDTM incorporated into the polymer begins to increase.

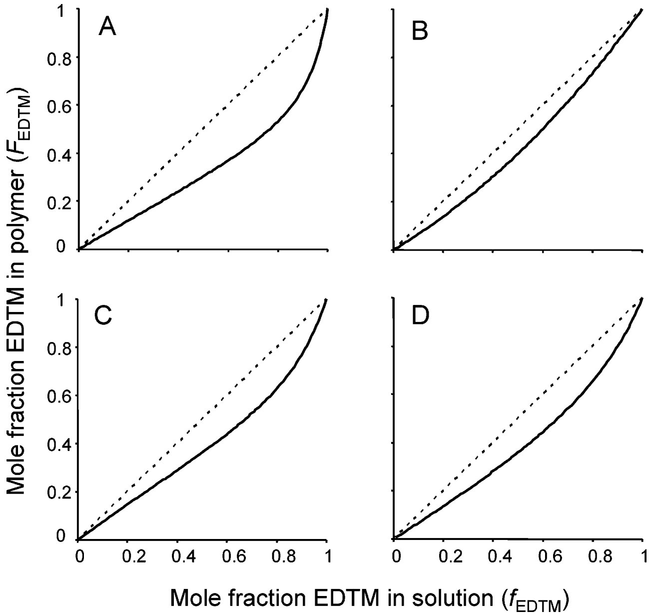

Figure 7. Copolymer composition curves for the electrochemical copolymerization of EDOT and EDTM on ITO. The solid lines correspond to reactivity ratios obtained by solution depletion measurements at low (A) and high (B) conversion, obtained by absorbance measurements (C), and the overall mean (D) of all experiments. The dotted lines show what would be observed if the mole fractions of EDTM in the feed solution and in the polymer were equal ($f = F$).

Figure 7C shows the copolymer compositions determined spectroscopically (Table 2) using the procedure described above. Figure 7D shows the copolymer composition using the mean reactivity ratios of $r_1 = 1.5$ and $r_2 = 0.4$. The plots are similar, showing a preference for incorporation of EDOT at all monomer concentrations. The similarities are not surprising, since the reactivity ratios obtained via changes in film absorptivity are an ensemble measurement of bulk film properties over a range of surface coverages and thus would mask differences at low and high surface coverages.

Conclusions

The presence of EDTM in copolymer films composed of EDOT and EDTM significantly alters their electrooptical properties. Spectroelectrochemical studies show significant increases in the electrooptical contrast, λ_{max}, and $E°$ with increasing solution mole fraction of EDTM (f_{EDTM}). The degree of EDTM functionalization of these copolymers depends on the initial monomer concentrations and the relative reactivity of the two monomers. This work has elucidated these relationships for EDOT and EDTM and has additionally shown that, in the case of electropolymerization, differences in the overpotential required to initiate polymer growth at the electrode surface can have significant effects on the relative amount of each monomer incorporated into the polymer. Mean reactivity ratios of 1.5 ± 0.2 and 0.4 ± 0.3 for r_1 (EDOT) and r_2 (EDTM) indicate that EDOT is preferentially incorporated into the copolymer at equimolar feed solution concentrations. However, over a broad range of comonomer feed concentrations, both monomers will be incorporated into the copolymer with a nonrandom microstructure that tends toward alternation of monomer units. Related studies, using potential-modulated attenuated total reflectance spectroscopy (PM-ATR),[1] show how important the EDTM/EDOT ratios are in determining effective electron-transfer rates and electrochromic switching rates, especially at the ITO/polymer interface. These results become especially significant in those cases where electrode modification using copolymers of PEDOT and PEDTM, or related PEDOT polymers (e.g., those with carboxylic acid side chains) is attempted, to optimize electron-transfer processes at ITO and related electrodes.[34]

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