Tuning the Electrochromic Properties of Poly(alkyl-3,4-ethylenedioxyselenophenes) Having High Contrast Ratio and Coloration Efficiency

Mao Li, Yana Sheynin, Asit Patra, and Michael Bendikov*

Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, 76100 Israel

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A systematic study of the electrochemical, spectroelectrochemical and electrochromic (EC) properties of poly(alkyl-3,4-ethylenedioxyselenophene) (PEDOS-C_n) ($n = 0$, 2, 4, 6, 8 and 12) films is reported. The alkyl substituents lead PEDOS-C_n films to exhibit sharper redox peaks than the parent PEDOS film and raise an onset of their oxidation potentials by 0.20−0.62 V. As expected, the introduction of alkyl chains significantly improves the EC properties and the electrochemical stability of PEDOS-C_n films and results in high contrast ratios and coloration efficiencies, low switching voltages, and fast switching times. As the length of the alkyl chain increases, the broad absorption peak of PEDOS sharpens and splits into three distinct peaks for PEDOS-C_n films starting from $n = 4$. We have identified the correlations between EC properties (such as coloration efficiency) and other observed properties of PEDOS-C_n films (such as their peak width, the position of the maximum absorption peak, the ratio of the absorption intensity of NIR spectra peaks to visible spectra peaks) and the contrast ratio. Interestingly, EC properties show bell-shaped behavior as a function of alkyl chain length, which reaches the maximum for PEDOS-C_6 film, whereas the EC properties of films with shorter and longer alkyl chains are poorer.

Introduction

The color change induced in materials by the electrochemical doping/dedoping processes can be applied to the fabrication of electrochromic (EC) displays or windows.[1] Initial studies of EC materials began with inorganic compounds such as tungsten trioxide (WO_3) and iridium dioxide (IrO_2);[1a] however, most recent studies on EC materials are devoted to conducting polymers because of their superior EC properties, such as better processability, faster switching, and color tenability.[1b] Very recently, electrochromic behavior of a self-propagating ~25 nm thick molecular-based assembly has been reported.[2] Various conducting polymers have been developed as EC materials, such as polythiophenes,[1b,3] polypyrroles,[4] polycarbazoles,[5] and polyaniline.[6] Electropolymerized poly(3,4-ethylenedioxythiophene) (PEDOT)[7] and its derivatives have attracted increasing attention owing to their high contrast ratio (the change in percent transmittance between their colored neutral and bleached doped states), high coloration efficiency (CE) (the efficiency of the color changes that occur in response to applied charge) and good stability.[1b,8−11] The contrast ratio and the CE of parent PEDOT are 54% and 137 cm^2/C, respectively at full switch[9] and some conducting polymers based on PEDOT derivatives show even higher contrast ratios and CE values.[12−14] Of the PEDOT derivatives, the alkyl substituted PEDOT-C_8 and

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* Corresponding author. E-mail: michael.bendikov@weizmann.ac.il.

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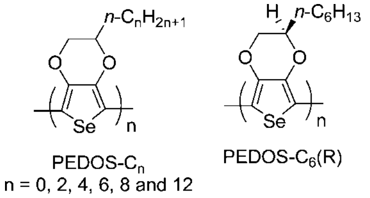
Scheme 1. Structures of PEDOS-C_n ($n = 0, 2, 4, 6, 8$, and 12) Films Studied in This Work



PEDOT-C_{14} show better contrast ratios and switching speeds than the parent PEDOT.[8] This has been explained by the long alkyl chains separating the polymer backbones from one another, which facilitates a more expanded morphology and allows the counterions to transport more easily within the film.[8] The stability of the EC materials is another crucially important feature for practical applications; PEDOT-C_8 and PEDOT-C_{14} films show the improved stability.[8] Although the structural modification of PEDOT to achieve enhanced EC properties has been studied extensively,[8−10,13,14] no systematic study has been reported on the effect of structural modifications of PEDOT derivatives in general and of alkyl groups in particular on EC properties.

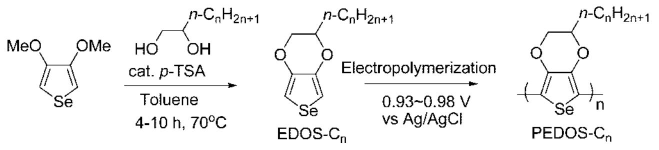
Recently, our group developed poly(3,4-ethylenedioxyselenophene) (PEDOS),[15] which contains a novel building block for conjugated polymers. PEDOS has a smaller band gap (E_g) (~1.4 eV) than PEDOT (~1.6 eV).[7,15] In a recent communication, we have also reported that PEDOS and PEDOS-C_6 films have excellent EC properties[16] that are superior to those of PEDOT. Following our discovery of the excellent EC properties of PEDOS-C_6 and considering that alkyl groups are currently the best substituents for enhancing the EC properties of conjugated polymers, we decided to study a series of poly(alkyl-3,4-ethylenedioxyselenophene) (PEDOS-C_n) ($n = 0, 2, 4, 6, 8$, and 12) derivatives (Scheme 1). Here, we report the systematic study of the dependence of the electrochemical, spectroelectrochemical and EC properties of PEDOS-C_n films on alkyl chain length. Interestingly, we find EC properties to rise and fall in a bell-shaped manner with increasing alkyl chain length.

Experimental Section

Synthesis of EDOS-C_n and PEDOS-C_n. All chemicals were purchased from the Sigma-Aldrich or ABCR chemical companies. The monomers EDOS-C_n were synthesized according to the general procedure given below, which is similar to the procedure published earlier (see Scheme 2).[15,16] High-resolution mass spectra were measured on a Waters Micromass GCT Premier mass spectrometer using field desorption (FD) ionization.

A mixture of 3,4-dimethoxyselenophene[15] (250 mg, 1.31 mmol), 1,2-alkyldiol (6.55 mmol, 5 equiv.), and a catalytic amount of *p*-toluene sulfonic acid (30 mg) was stirred in dry toluene (45 mL) at 70 °C until no starting material was detected by thin layer chromatography (TLC) ($t = 4-10$ h). The resulting dark colored mixture was concentrated under reduced pressure and the residue was diluted with water (50 mL). The mixture was extracted with hexane (3 × 50 mL). The combined organic layers were rinsed with H_2O, brine, dried ($MgSO_4$), and then concentrated. Purification of the crude residue by chromatography on silica gel (60−230 mesh; hexanes as eluent) gave EDOS-C_n.

Scheme 2



We note that as chain length increases, the EDOS-C_n compound yields increase significantly from about 52% for EDOS to 95% for EDOS-C_{12}.

EDOS-C_2. Yield: 60%. Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): 1.03 (t, $J = 7.5$ Hz, 3H), 1.60−1.70 (m, 2H), 3.83 (dd, $J = 11.25$ Hz, $J = 8$ Hz, 1H), 4.1 (dd, $J = 11$ Hz, $J = 4$ Hz, 1H), 3.95−4.06 (m, 1H), 6.73 (s, 2H). ^{13}C NMR (C_6D_6, 100 MHz): 9.15, 23.60, 67.45, 74.30, 101.37, 101.41, 143.09, 143.53. MS (M^+, ESI) 217.96. HRMS for $C_8H_{11}O_2Se$ [MH^+] calcd, 218.9924; found, 218.9928.

EDOS-C_4. Yield: 78%. Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): 0.91 (t, $J = 7$ Hz, 3H), 1.34−1.61 (m, 6H), 3.83 (dd, $J = 8.5$ Hz, $J = 3$ Hz, 1H), 4.07 (dd, $J = 7$ Hz, $J = 2$ Hz, 1H), 4.01−4.10 (m, 1H), 6.73 (s, 2H). ^{13}C NMR (C_6D_6, 100 MHz): 13.80, 22.33, 26.84, 30.19, 67.78, 73.16, 101.39, 101.41, 143.10, 143.56. HRMS for $C_{10}H_{14}O_2Se$ [M^+] calcd, 246.0159; found, 246.0152.

Chiral-EDOS-C_6 (EDOS-C_6(R)). Yield: 54%. Colorless oil. Chiral R-1,2-octyldiol was used. The NMR data for EDOS-C_6(R) are identical to racemic EDOS-C_6.[16] ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.89 (t, 3H), 1.20−1.40 (m, 8H), 1.50−1.70 (m, 2H), 3.83 (dd, $J = 11.7$ Hz, 8.5 Hz, 1H), 4.02−4.14 (m, 2H), 6.75 (s, 2H). HRMS for $C_{12}H_{18}O_2Se$ [M^+] calcd, 274.0472; found, 274.0468.

EDOS-C_8. Yield: 91%. Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): 0.86 (t, $J = 6.25$ Hz, 3H), 1.25−1.56 (m, 14H), 3.83 (dd, $J = 11.75$ Hz, $J = 8.5$ Hz, 1H), 4.09 (dd, $J = 11.75$ Hz, $J = 2.25$ Hz, 1H), 4.01−4.10 (m, 1H), 6.73 (s, 2H). ^{13}C NMR (C_6D_6, 100 MHz): 14.10, 22.82, 24.96, 29.36, 29.50, 29.53, 30.53, 31.98, 67.80, 73.19, 101.41, 101.44, 143.12, 143.57. HRMS for $C_{14}H_{22}O_2Se$ [M^+] calcd, 302.0785; found, 302.0805.

EDOS-C_{12}. Yield: 95%. White solid. Mp: 34 °C. ^{1}H NMR ($CDCl_3$, 250 MHz). 0.86 (t, $J = 6.25$ Hz, 3H), 1.24−1.56 (m, 22H), 3.83 (dd, $J = 11.5$ Hz, $J = 8.5$ Hz, 1H), 4.09 (dd, $J = 11.75$ Hz, $J = 2.25$ Hz, 1H), 4.01−4.09 (m, 1H), 6.73 (s, 2H). ^{13}C NMR (C_6D_6, 100 MHz): 14.12, 22.87, 24.98, 29.54, 29.58, 29.62, 29.75, 29.86, 29.87, 29.89, 30.54, 32.09, 67.81, 73.19, 101.42, 101.44, 143.12. 143.57. HRMS for $C_{18}H_{30}O_2Se$ [M^+] calcd, 358.1411; found, 358.1426.

Synthesis and characterization of EDOS[15] and EDOS-C_6[16] have been reported earlier.

Synthesis of EDOT-C_6 for Comparative Purposes. 3,4-Dimethoxythiophene (2.0 g, 13.9 mmol), octanediol (5.07 g, 34.7 mmol), and *p*-toluenesulfonic acid (86 mg 0.45 mmol) were dissolved in dry toluene (110 mL) and heated for 3 days at 90 °C (while monitoring by TLC). After the solution was cooled to room temperature, 30 mL water was added and the product was extracted with ether. The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed. The resulting oil was purified by column chromatography (hexane, ethyl acetate). Yield: 2.58 g, 82%. ^{1}H NMR ($CDCl_3$, 250 MHz): 0.87 (t, $J = 7.0$ Hz, 3H), 1.28−1.33 (m, 8H), 1.50−1.64 (m, 2H), 3.81−3.87 (dd, 7.9 Hz,

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Table 1. Electrochemical and Electrochromic Data of PEDOS-C$_n$ Films

			λ_{max}(nm)							
polymers	E_{onset}^a (V)	$E_{1/2}^b$ (V)	middle^c	right^d	R^e	L^f (nm)	E_g^g (eV)	CR^h ΔT (%)	CE^i (cm^2/C)	switching time (s)^j
PEDOS	−0.95	−0.49	666		0.93	279	1.42	55	212	0.6
PEDOS-C$_2$	−0.75	−0.67	688	752	0.84	236	1.46	70	243	0.6
PEDOS-C$_4$	−0.52	−0.48	685	761	0.58	183	1.54	77	369	0.5
PEDOS-C$_6$	−0.55	−0.46	686	763	0.39	174	1.54	89	715^k	0.7
PEDOS-C$_6$(R)	−0.54	−0.44	687	764	0.45	178	1.54	79	612	0.6
PEDOS-C$_8$	−0.33	−0.25	684	760	0.48	178	1.55	76	400	0.5
PEDOS-C$_{12}$	−0.37	−0.36	680	755	0.62	190	1.55	67	219	0.6

[a] The oxidation onset potential of PEDOS-C$_n$ film. [b] The redox potential $E_{1/2} = (E_{pa} + E_{pc})/2$. [c] The central absorption peak of the neutral polymer film. [d] The longest wavelength absorption peak of the neutral polymer film. [e] The ratio of the absorption intensity at 1600 nm of the doped state (0.5 V) of the polymer film to the maximum absorption intensity in the visible range of the neutral state (−0.9 V) of the polymer film ($I_{abs}(\lambda_{1600})/I_{abs}(\lambda_{max})$). [f] The peak width of the absorption peak at the half height of the central peak of the neutral polymer film. [g] The band gap was calculated using the onset of the longest wavelength absorption peak of the neutral state of the film. [h] CR is the contrast ratio, $T_b(\lambda) - T_c(\lambda)$, where T_b and T_c are the transmittance in the bleached and colored states at λ_{max} of the longest wavelength absorption peak in the neutral state of the film. [i] CE is the coloration efficiency.[19] [j] The switching time from the neutral state to the doped state of the polymer film i.e. the time required to reach 95% of the maximum contrast ratio. [k] A coloration efficiency of 686−773 cm^2/C was routinely obtained in several experiments.[16]

3.3 Hz, 1H), 4.07−4.14 (m, 2H), 6.28 (s, 2H). The ^{1}H NMR data are similar to those reported in ref 17.^{13}C NMR (C_6D_6, 100 MHz): 14.01, 22.65, 24.88, 29.12, 30.05, 31.69, 68.12, 73.50, 99.33 (two carbons), 142.17, 142.60. HRMS for $C_{12}H_{18}O_2S$ [M$^+$] calcd, 226.1028; found, 226.1031. Oil.

Electrochemistry and Spectroelectrochemistry. Electrochemical studies were carried out with a Princeton Applied Research VF263A potentiostat, using an indium tin oxide (ITO)-coated glass slide as the working electrode (7 × 50 × 0.7 mm, R_S = 8−12 Ω/□, Delta Technologies Inc.), a gold flag as the counter electrode, and an AgCl coated Ag wire, which was directly dipped in the electrolyte solution,[18] as the reference electrode. The $E_{1/2} = (E_{pa} + E_{pc})/2$ of the Fc/Fc$^+$ couple is 0.24 V vs Ag/AgCl under these conditions. The electrolyte used was 0.1 M $LiBF_4$ in propylene carbonate (PC). The PEDOS-C$_n$ films were prepared on ITO-coated glass slides (~0.7 cm × 3.2 cm) in electrolyte at constant potentials of 0.93−0.98 V from a 0.01 M monomer solution in 0.1 M $LiBF_4$/PC, which was bubbled with nitrogen before use to remove any incipient oxygen. Before examining the optical properties of PEDOS-C$_n$ films, the films were rinsed with acetonitrile. UV−vis-NIR spectra were recorded on a V-570 JASCO UV−vis−NIR spectrophotometer. In spectroelectrochemical measurements, the working electrode was an ITO-coated glass slide, the counter electrode was a platinum wire, and Ag/AgCl was used as the pseudoreference electrode.

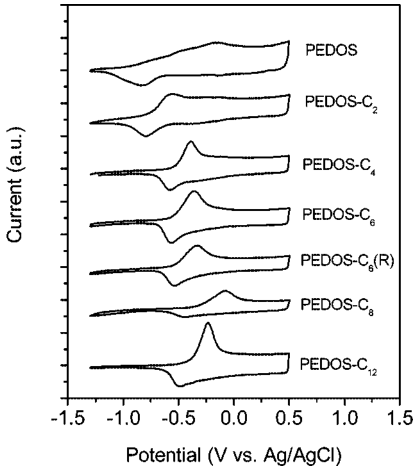

Figure 1. Cyclic voltammetry of PEDOS-C$_n$ (n = 0, 2, 4, 6, 8, and 12) films prepared at constant potentials using an electrodeposition charge of 50 mC (30 mC for PEDOS) at a scan rate of 20 mV/s in 0.1 M $LiBF_4$/PC.

Results and Discussion

The monomers EDOS-C$_n$ (n = 0, 2, 4, 6, 8 and 12) were electropolymerized using constant potentials of 0.93−0.98 V vs Ag/AgCl and passing charge of 30 mC (n = 0) and 50 mC (n = 2, 4, 6, 8 and 12) in 0.1 M $LiBF_4$/PC to form highly electroactive PEDOS-C$_n$ films on ITO electrodes (Table 1).

Figure 1 shows cyclic voltammetric data of PEDOS-C$_n$ films measured on ITO electrodes in monomer-free electrolyte. The PEDOS film exhibits broad redox peaks extending from −0.84 to −0.14 V. The oxidation onset potential of PEDOS is −0.95 V and its $E_{1/2}$ is −0.49 V, which is 0.1 V lower than that of PEDOT film.[20] This implies that the EC switching potentials of PEDOS film are lower than those of PEDOT film. The PEDOS-C$_2$ film gives rise to the formation of narrower redox peaks extending from −0.80 to −0.56 V, followed by a broad shoulder and a capacitive current at more positive potentials. The oxidation onset potential of PEDOS-C$_2$ is −0.75 V, which is higher than the oxidation onset potential of PEDOS. Films having considerably increased alkyl chain lengths, the PEDOS-C$_n$ (n = 4, 6, 8, and 12) films, have even narrower redox peaks and higher oxidation potentials, probably because of the higher resistance resulting from the alkyl chains. As alkyl chain length increases, the onset of the oxidation potentials of PEDOS-C$_n$ films positively shift from −0.95 to −0.30 V (Table 1 and Figure 1), which shows the strong effect of alkyl chains on the electrochemical behavior of PEDOS-C$_n$ films. We note that the $E_{1/2}$ values for PEDOS-C$_n$ films generally increase with increasing alkyl chain lengths (although the $E_{1/2}$ of PEDOS-C$_8$ is unusually high). The onset of oxidation potentials of PEDOS-C$_n$ (n = 8 and 12) show a positive shift of 0.18 V to 0.22 V

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(19) Coloration efficiency, in units of cm^2/C at a specified wavelength, can be expressed as $CE(\lambda) = \Delta OD/Q_d$. The values of these terms are obtained by determining the injected/ejected charge as a function of the electrode area (expressed in terms of charge density (Q_d) in units of C/cm^2) and by determining the change in optical density (ΔOD) (which is obtained from the chromoabsorptometry and chronocoulometry data acquired from the redox step of the polymer). ΔOD at a specified wavelength is expressed as $\triangle OD = \log[T_b(\lambda)/T_c(\lambda)]$, where T_b and T_c are the transmittance in the bleached and colored states, respectively. See refs 1a,1e, and 9.

(20) The redox potential of PEDOT film is −0.39 V under the same conditions.

relative to PEDOS-C_6 mainly due to the greater resistance resulting from long alkyl chains between the polymer backbones (Table 1). These long chains also cause the polymer backbones to separate from each other, which leads PEDOS-C_n films to exhibit sharper (more reversible) redox peaks, implying faster doping/dedoping processes. This separation facilitates a more expanded morphology and allows easy transport of the counterions within the film, which favors fast switching[10b,21] and indicates that EC properties will be affected strongly by alkyl chain length.

The EDOS-C_n monomers were electropolymerized on ITO and the resulting PEDOS-C_n films were rinsed with acetonitrile and then placed into UV−vis−NIR quartz cells. Spectroelectrochemical data were recorded at various applied potentials *in situ*. Figure 2 shows the absorption spectra in the UV−vis−NIR region of PEDOS-C_n films at applied potentials between −0.9 and 0.5 V. The absorption of PEDOS film exhibits a broad peak (with a peak width at half height (L) of 279 nm) (Table 1) with $\lambda_{max} = 666$ nm in the neutral state (−0.9 V), which corresponds to a distinctive π to π^* transition (Figure 2a), and contains two scarcely discernible shoulder peaks at shorter and longer wavelengths.[15] In the neutral state, a comparison of the absorption spectra of PEDOS-C_n films reveals important differences in the shapes of the absorption peaks. As shown in Figure 2b, the PEDOS-C_2 film has a somewhat sharper absorption peak (with a peak width at half height (L) of 236 nm) with $\lambda_{max} = 688$ nm, this being a red-shift of 22 nm compared to PEDOS. As the alkyl chain length increases (Figure 2c,d,f,g), the absorption peaks of PEDOS-C_n (n = 4, 6, 8, and 12) films split into three distinct peaks, with the longest wavelength peak becoming the most intense (λ_{max} = 755 to 764 nm). In contrast to the broad absorption band observed for the parent PEDOS film, the absorption spectra of PEDOS-C_n (n = 4, 6, 8, and 12) films contain sharper peaks (with a peak width at half height (L) of 174−190 nm), see Table 1. However, we note that the splitting of the UV−vis absorption band and the longest wavelength absorption peak for n = 4, 6, 8, and 12 is simply a result of the observed vibronic progression. Indeed, the difference between newly observed peaks is about 1460−1470 cm^{-1}, which corresponds to the C−C stretching frequency of the carbon backbone in polyselenophenes.[22] Previously, it was suggested that in conjugated polymers, larger vibronic splitting correlate with more rigid structure.[23] The sharpening of the visible absorption bands in the PEDOS-C_n series shows that the length of the alkyl substituents has a significant effect on the polymer structure, probably due to weakening the interaction between the PEDOS-C_n backbones. We recall also that sharper redox peaks are observed for longer chain lengths in PEDOS-C_n films (Figure 1).

The band gap (E_g), defined as the onset of the π to π^* transition of the neutral PEDOS film, was calculated to be 1.42 eV (873 nm),[16] which is lower than the E_g of PEDOT[7,9] by 0.18−0.28 eV (the λ_{max} of PEDOS is red-shifted by 81 nm compared to the λ_{max} of PEDOT[7,9] film). As the length of the alkyl chains increases, the onset of the UV−vis absorption of PEDOS-C_n films shifts to shorter wavelengths and then stays practically constant. We note, however, that the λ_{max} of the central peak undergoes significantly smaller changes in wavelength as a function of alkyl chain length. The observed formal increase in the optical band gap of PEDOS-C_n does not correspond to shorter conjugation lengths as a result of alkyl substituents, but rather originates in a more narrow UV spectrum and consequently in an onset at a shorter wavelength. As expected, according to PBC/B3LYP/6-31G(d) calculations performed in the gas phase, the band gap of PEDOS-C_n does not change with alkyl chain length[16] because the alkyl chains do not affect the electronic structure of polymers. So, possibly, the observed differences in the UV−vis spectra of PEDOS-C_n films are mostly due to changes in the interactions between the polymer chains, which depend on alkyl chain length (with weaker interactions between the backbones having long alkyl chains). Second option is that in neutral polymers, red-shifted λ_{max} values and narrower absorption peaks can correspond to a larger conjugation length because of either higher molecular weights or to better solid-state ordering, leading to an ideally planar structure. We cannot distinguish between these two options; however, in either event, red-shifted λ_{max} values and narrower absorption peaks are favorable for electrochromic devices (and they lead to a shorter onset and consequently formally larger band gap).

The lower band gap (and lower oxidation potentials) of polyselenophenes compared to the corresponding polythiophenes requires lower switching potentials, so that polyselenophene films should require less power for EC switching. More importantly, the red-shift of λ_{max} in PEDOS-C_n films compared to PEDOT and PEDOT derivatives leads to the absence of absorption (i.e., to near-complete transmittance) between 400 and 500 nm, which yields a pure blue color.[24]

As the potential applied to film increases, the broad absorption peaks at about 1050 and 1600 nm, which correspond to polaron and bipolaron species, respectively, also increase. While the absorption intensity of PEDOS film at around 1000 nm continuously increases upon doping, the absorption intensity of alkyl-substituted PEDOS-C_n derivatives increases upon initial doping and then decreases upon successive doping (Figure 2). The ratio of absorption in the NIR (1600 nm) to the peak maximum of the π−π^* transition of the neutral polymer ($I_{abs}(\lambda_{1600})/I_{abs}(\lambda_{max})$) is around 0.93 for PEDOS, decreases to 0.39 for PEDOS-C_6, and then increases again to 0.62 for PEDOS-C_{12} (Table 1).

The optical switching of PEDOS-C_n films was examined at λ_{max} of the right-most and longest wavelength peak. Table

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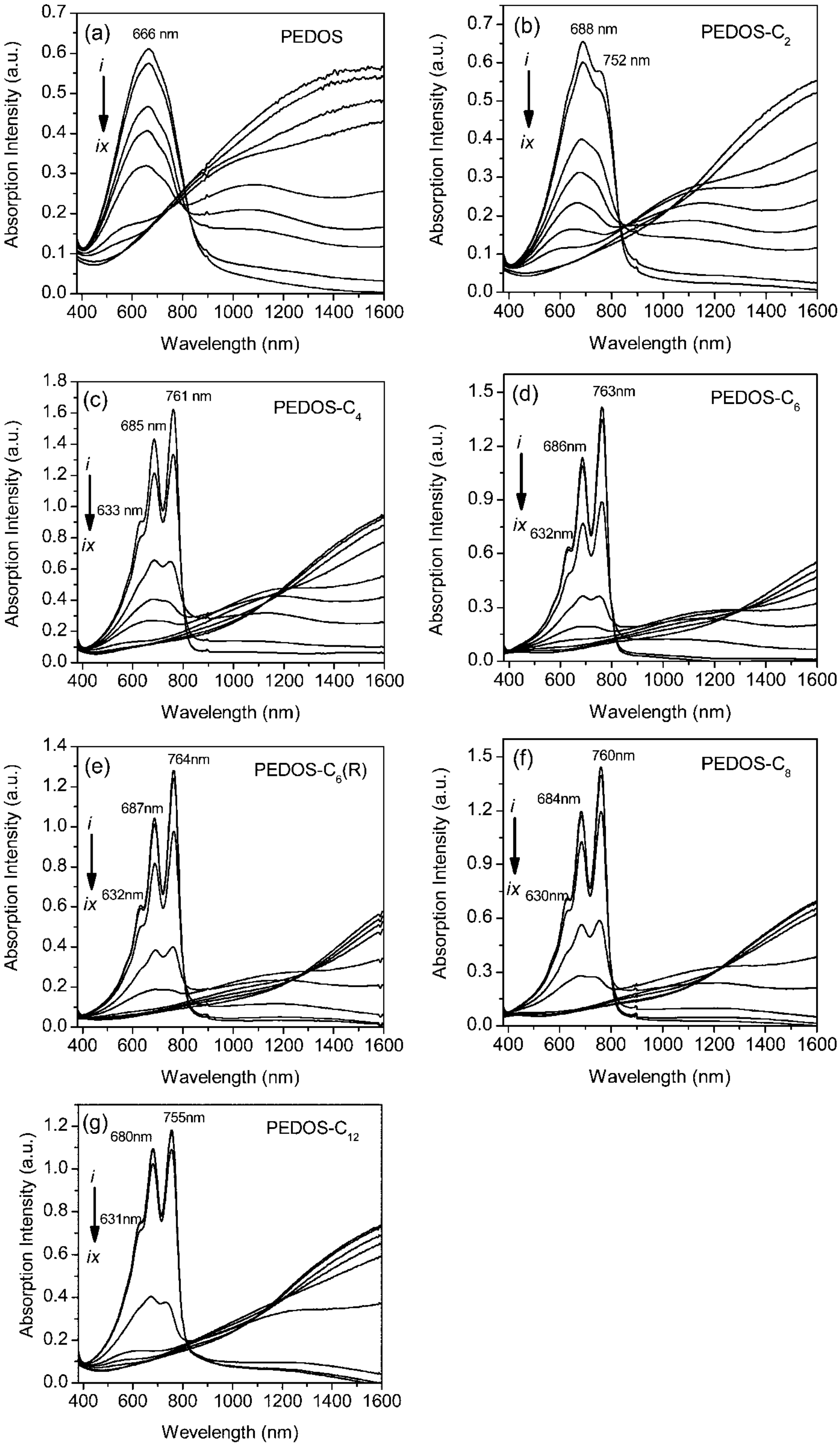

Figure 2. Spectroelectrochemical data for PEDOS-C$_n$: (a) $n = 0$;[16] (b) $n = 2$; (c) $n = 4$; (d) $n = 6$;[16] (e) $n = 6$ (chiral(R)); (f) $n = 8$; and (g) $n = 12$ films prepared on ITO-coated glass slides and measured at applied potentials of (i) −0.9, (ii) −0.7, (iii) −0.5, (iv) −0.3, (v) −0.1, (vi) 0, (vii) 0.1, (viii) 0.3, and (ix) 0.5 V, vs Ag/AgCl.

1 shows switching studies on 100−150 nm thick films (as determined by a Dektak 5 M Manual Veeco Instrument) of PEDOS-C$_n$ on ITO-coated glass slides when the potentials were stepped between −0.9 V and +0.5 V in 0.1 M LiBF$_4$/PC. As shown in Table 1, the PEDOS film exhibits a contrast ratio of 55% and a CE of 212 cm^2/C.[16,19] The EC properties of PEDOS are better than those of PEDOT, which has a contrast ratio of 54% and a CE of 137 cm^2/C under similar conditions (full switch).[9] As the length of the alkyl chains increases, the contrast ratio and the CE improve very significantly. The CE value of PEDOS-C$_6$ film on ITO in solution is 686−773 cm^2/C.[16] These improved EC properties

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(24) For the photo of PEDOS-C$_6$ film, see ref 16.

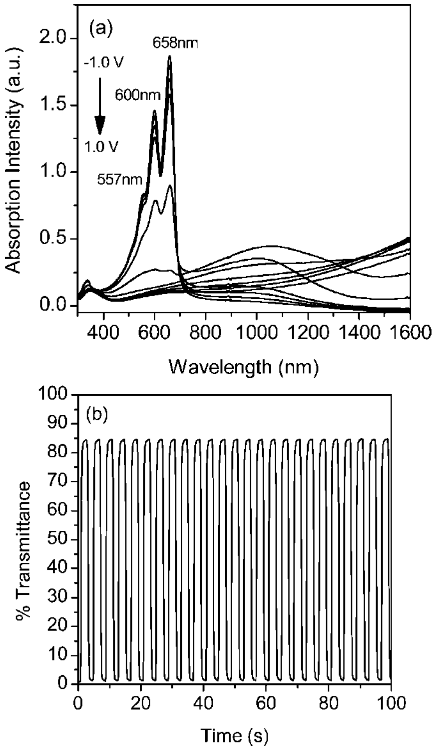

Figure 3. (a) Spectroelectrochemistry of PEDOT-C_6 film when it was stepped between −1.0 and 1.0 V vs Ag/AgCl at 0.2 V intervals, and (b) the percent transmittance monitored at 658 nm for the switching between −1.0 and 1.0 V at intervals of 2 s for PEDOT-C_6 film.

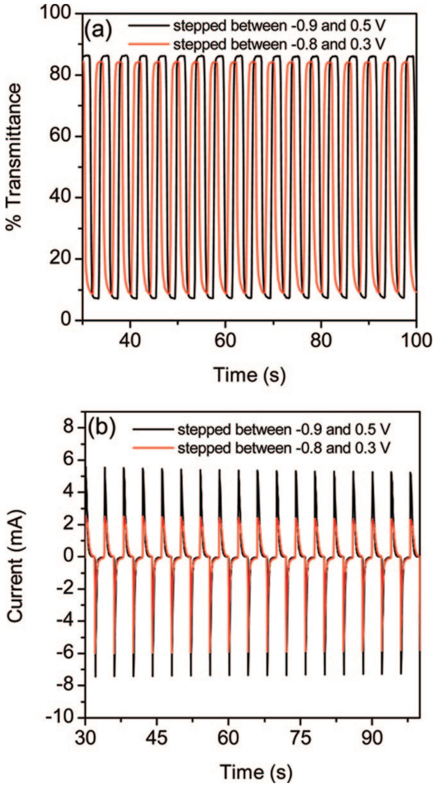

Figure 4. Switching studies of (a) percent transmittance monitored at 764 nm and (b) switching current for PEDOS-C_6(R) film, when it was stepped between −0.9 and 0.5 V (black lines) and between −0.8 and 0.3 V (red lines) vs Ag/AgCl at 2 s intervals.

are in line with the decreased absorption ratios of these materials in the NIR region relative to the visible spectrum ($I_{abs}(\lambda_{1600})/I_{abs}(\lambda_{max})$) and also with the decrease in peak width at the half height of the central peak (L) (Table 1). Low absorption in the NIR region has been related to low conductivity and also improved EC properties.[21] This is in line with conductivity measurements for PEDOT-C_n, which show PEDOT-C_6 films to have the lowest conductivity in the PEDOT-C_n series of films (n = 0, 1, 6, 10, and 14).[25] The poorer EC properties of the PEDOS-C_8 and PEDOS-C_{12} films, which have very long alkyl chains probably stem from overly large distances between the polymer backbones leading to inefficient charge accumulation. A switching time (the time required to reach 95% of the maximum contrast ratio) of 0.5−0.7 s was measured for all PEDOS-C_n films. As shown in Table 1, we did not find a big difference in switching times between any of the PEDOS-C_n films. Finally, PEDOS-C_6 has a very high contrast ratio of 88−89% when stepped between −0.9 and 0.5 V. This contrast ratio is similar to the highest reported $\Delta\%T$ of 89% for dibenzyl poly(3,4-propylenedioxythiophene) (PProDOT-Bz_2), which has a CE of 575 cm^2/C when stepped between −1.0 and 1.0 V.[13] The contrast ratios of PEDOS-C_n films show a similar trend to that of coloration efficiency, with a maximum at PEDOS-C_6 (Table 1). Both the contrast ratio and the CE of PEDOS-C_6 are among the highest reported, making it a unique EC material.[16]

For comparative purposes, PEDOT-C_6 film was prepared. The λ_{max} of PEDOT-C_6 appears at 658 nm (Figure 3a), which is similar to values previously[17] reported. The PEDOT-C_6 film has a contrast ratio of 83% (Figure 3b) and a CE of 491 cm^2/C ($T_b\% = 84.64$, $T_c\% = 1.29$, and $Q_d = 3.70$ mC/cm^2). These are the highest reported values for any PEDOT-C_n[8] film, but are still lower than the values achieved by PEDOS-C_6 film, which show the best EC properties compared to other PEDOS-C_n films we prepared (Table 1).

In addition, we obtained the PEDOS-C_6(R) film by electropolymerization of the chiral monomer EDOS-C_6(R). Our aim was to prepare a film with a more ordered structure compared to the film obtained from racemic EDOS-C_6 and, consequently, we expected an improvement in EC properties. However, we found that PEDOS-C_6(R) film exhibits an absorption spectrum (Figure 2e) and EC properties (contrast ratio of 79% and CE of 612 cm^2/C) that are at best similar to, and at worst, poorer than those of racemic PEDOS-C_6 (Table 1). This is most probably due to the regiorandom structure of the polymer (so that the presence of a single stereoisomer does not improve its EC properties).

The CE can be increased by decreasing the switching window (doping/dedoping levels).[9,14b] As shown in Figure 4, switching between −0.8 and 0.3 V (instead of between −0.9 and 0.5 V) leads to a slight decrease in the contrast ratio to 76% and an increase in the CE to 680 cm^2/C.

A long-term stability study of PEDOS-C_n films was carried out by measuring the maximum contrast ratio as a function of the number of switching cycles for the films on an ITO-coated glass slide in an electrochemical cell opened to the air without purging. The PEDOS-C_n films were fully switched by stepping the potentials between −0.9 and 0.5

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(25) Groenendaal, L.; Zotti, G.; Jonas, F. *Synth. Met.* **2001**, *118*, 105–109.

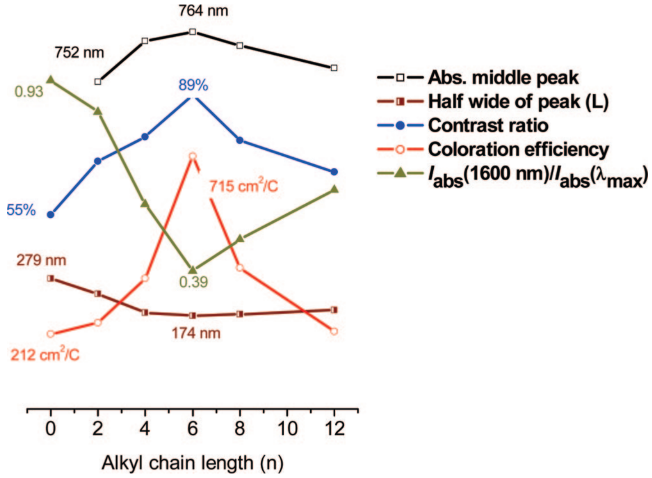

Figure 5. Correlations of the optical and electrochromic properties of PEDOS-C_n films with alkyl chain length.

V. The contrast ratios of PEDOS, PEDOS-C_2, PEDOS-C_4, PEDOS-C_6, PEDOS-C_8 and PEDOS-C_{12} films remain at about 60% of the maximum contrast ratio after 2000, 5000, 10000, 10000, 500, and 12000 double switches, respectively, so as the length of the alkyl chains increases, the electrochemical stability improves and is comparative with that of PEDOT-C_n films.[8] The PEDOS-C_8 film is an exception that exhibits poor stability, probably due to the polymer with C_8 alkyl chains being more easily dissolved in solution during long-term stability testing. We note that CV data for PEDOS-C_8 (Figure 1) is also somewhat different from other PEDOS-C_n films.

The PEDOS-C_6 film presents the best EC properties of all the PEDOS-C_n films. Figure 5 summarizes the different properties of the PEDOS-C_n films that we measured as a function of alkyl chain length. Interestingly, all properties show bell-shaped behavior with the most extreme value always occurring at $n = 6$. Many parameters behave similarly to CE and, in order to achieve a high CE, not only does the contrast ratio need to be maximized, but the ratio of the NIR absorption peaks to the visible spectrum absorption peak ($I_{abs}(\lambda_{1600})/I_{abs}(\lambda_{max})$) needs to be minimized, which relates to lower conductivity. In addition, we have identified parameters, such as the width of the absorption peak at the half height of the central peak of the neutral polymer film (L) and the λ_{max}, which also correlate with the CE (the peak width should be minimized and the λ_{max} should be maximized).

Conclusions

We prepared a series of PEDOS-C_n (n = 0, 2, 4, 6, 8, and 12) films by electropolymerization of the corresponding EDOS-C_n monomers bearing alkyl chains of different lengths and studied the effect of this most essential type of substituent (alkyl chains) on the very promising class of EC materials that is polyselenophenes. The broad absorption peak of parent PEDOS sharpens and splits into three distinct peaks for PEDOS-C_n films starting from $n = 4$. The absorption of all PEDOS-C_n films is red-shifted by 80−100 nm compared to PEDOT-C_n films.[8] The red-shift of the λ_{max} of PEDOS-C_n films compared to PEDOT and its derivatives leads to the near-absence of absorption (complete transmittance) between 400 and 500 nm. This causes the material to have a pure blue color. As expected, the introduction of alkyl chains significantly improves EC properties and the electrochemical stability of the polymers. The PEDOS-C_n films show both high contrast ratios and high CE with low switching voltages, fast switching times and remarkable stability. Interestingly, the coloration efficiencies show bell-shaped behavior relative to alkyl chain length and reach their maximum values for PEDOS-C_6 films, whereas other PEDOS-C_n films with shorter and longer alkyl chains exhibit poorer coloration efficiencies. Intriguingly, other properties of the PEDOS-C_n films (their contrast ratio, λ_{max}, peak widths, and the ratio of the absorption intensity peak at NIR wavelengths to the absorption intensity peak in the visible spectrum) were measured as a function of alkyl chain length and all also show bell-shaped behavior with the most extreme value always at $n = 6$.

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