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Major Effect of Electropolymerization Solvent on Morphology and Electrochromic Properties of PEDOT Films

Elena Poverenov,[†,‡] Mao Li,[†,‡] Arkady Bitler,[§] and Michael Bendikov*[,†]

[†]*Department of Organic Chemistry and* [§]*Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, 76100 Israel.* [‡]*These authors made an equal contribution to this work.*

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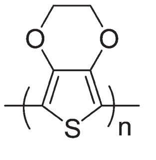
Although significant efforts were devoted to improving the properties of conductive polymers, the effects of solvent and supporting electrolytes on the morphology and electrochromic features of electropolymerized materials have been scantly investigated. In this work, the effects of the polymerization conditions, such as the solvents and supporting electrolytes, on the morphological structure and electrochromic properties of PEDOT films were systematically studied. Surprisingly, we find a very significant solvent effect and a small supporting electrolyte effect. We show that morphological properties also strongly correlate with electrochromic properties. Films prepared in propylene carbonate have a smoother structure than those prepared in acetonitrile and this leads to superior electrochromic properties, such as an exceptionally high contrast ratio (71%), transparency in the doped state (80%), and coloration efficiency (193 cm^2/C) for the films prepared in propylene carbonate. Significant differences between propylene carbonate and acetonitrile were explained by different solubilities of EDOT oligomers produced during initial stages of electropolymerization in these solvents.

Introduction

Conducting polymers[1,2] are widely studied for applications in photovoltaic cells,[3,4] chemical sensors,[5] light-emitting diodes (LEDs),[6] and field effect transistors (FETs).[7] Because of their excellent properties (high conductivity, high stability, transparency in the oxidized state, and relatively low band gap), poly(3,4-ethylenedioxythiophene) (PEDOT)[1] and its derivatives have developed into one of the most important materials from both fundamental and practical perspectives and are now utilized in several applications, such as LEDs, organic solar cells, and electrochromic devices.[8–11]



PEDOT

The electrochromism of conducting polymers is a subject of much interest and has a wide variety of applications.[12–14] Compared to inorganic materials, conducting polymers offer the benefits of a fast switching time,[15] high

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

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contrast ratio,[16−20] good processability,[21] and the ability to fine-tune the band gap by modifying the structure.[11,22] PEDOT and its derivatives are considered to be especially promising for electrochromic applications.[9] A significant amount of research, mostly originating from Reynolds' group,[22] was performed in recent years on the electrochromic properties of electrochemically prepared PEDOT films.[8a,9,10a,11a,14−25] The best reported contrast ratio and coloration efficiency[26] of PEDOT films are 54% and 183 cm^2/C, respectively.[23] PEDOT derivatives are also considered to be very promising transparent polymer electrodes and switchable electroactive materials.[8a,27] PEDOT:PSS transparent electrodes have performed successfully in some organic optoelectronic devices, showing an efficiency close to that of a classic ITO electrode.[28]

Morphology should influence the physical and electrochemical properties of polymer films. However, the factors governing the morphology of electrochemically prepared polymer films are still unclear and only a few groups have studied them with respect to PEDOT.[9,29−31] The effect of polymerization conditions, such as the applied potential, solvent, and supporting electrolyte on conductive polymer morphology has attracted significant attention;[29−31] however, systematic studies, which include concurrent variation of several polymerization conditions, are lacking. It was found that supporting electrolytes possessing small anions facilitate the formation of a more open morphology and low conductivity.[32,33] The doping level is also known to influence the contrast ratio and the coloration efficiency of electrochromic films.[18,23] A small supporting electrolyte may enhance the electrochromic properties[34] because the counterion can easily diffuse throughout the film, which leads to a high doping level and contrast ratio. Although significant efforts at improving the properties of conductive polymers were devoted mainly to structural modifications,[24,35,36] the effects of the solvent and supporting electrolytes on electrochromic features and the correlations between the morphology of electropolymerized materials and their electrochromic properties were never systematically investigated.

In the present work, we prepared a series of PEDOT films using various polymerization conditions, such as different solvents, supporting electrolytes, and electropolymerization techniques. The effect of electropolymerization conditions was studied by UV−vis−NIR spectroscopy, SEM, AFM, and through a comparison of the electrochromic properties of the resultant polymer films. A clear correlation between the morphology of the polymer film and its electrochromic properties was found. The solvent has a major influence on film properties (including electrochromic properties) and the effect of the applied potential is also quite significant, whereas the nature of the supporting electrolytes has only a small effect. During this work, PEDOT films with a high transparency in the doped state (80% at λ_{max} = 635 nm), contrast ratio (71%), and coloration efficiency (193 cm^2/C) were obtained. These contrast ratio and coloration efficiency values are significantly higher than previously reported.

Experimental Section

All chemicals were purchased from the Sigma-Aldrich chemical company.

Electrochemical studies were carried out with a Princeton Applied Research 263A potentiostat using an indium tin oxide (ITO)-coated glass slide as the working electrode (7 × 50 × 0.7 mm, $R_s = 8-12\ \Omega/\square$, Delta Technologies Inc.), a platinum wire as the counter electrode, and an AgCl coated Ag wire, which was directly dipped into the electrolyte solution,[37] as the pseudo reference electrode. Reported potentials were recalculated to the saturated calomel electrode (SCE) scale using an Fc/Fc$^+$ couple.

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(26) The coloration efficiency (CE; in units of cm^2/C) at a specified wavelength is expressed as $\mathrm{CE}(\lambda) = \Delta\mathrm{OD}/Q_d = A \times \log(T_1/T_2) \times 1000/(Q_1 + Q_2)$, where Q_d is the injected/ejected (Q_1 and Q_2) charge density (in units of C/cm^2), OD is an optical density, and T_1 and T_2 are the transmittance in the doped (bleached) and neutral (colored) states, respectively. A is a working electrode area. For details see: (a) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. In *Electrochromism: Fundamentals and Applications*; Wiley-VCH: Weinheim, Germany, 1995. (b) Bange, K.; Bambke, T. *Adv. Mater.* **1990**, *2*, 10.

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Under these conditions, the Fc/Fc$^+$ standard was calibrated to be 0.34 V.[38]

The PEDOT films were prepared by electropolymerization of EDOT (3,4-ethylenedioxythiophene) on ITO-coated glass slides (working area of 0.7 × 3.2 cm^2) using tetra-*n*-butylammonium perchlorate (TBAClO$_4$), tetra-*n*-butylammonium tetrafluoroborate (TBABF$_4$), LiClO$_4$, and LiBF$_4$ as supporting electrolytes, and propylene carbonate (PC) and acetonitrile (MeCN) as solvents. EDOT concentration was about 1×10^{-2} M. The solution was purged with nitrogen before polymerization to remove any incipient oxygen. The films were prepared at constant potential mode at 1.15−1.20 V vs SCE by passing a charge of 50 mC or in cyclic voltammetry mode by cycling from −1.0 to 1.4 V or from −1.0 to 1.6 V at a scan rate of 100 mV/s over 10−15 cycles. Before examining the optical properties of PEDOT films, we rinsed the films 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 pseudo reference electrode. The spectroelectrochemical measurements were performed in the same solvent and electrolyte as the preparation of PEDOT film.[39,40]

SEM images of PEDOT films on ITO slides were taken with a Leo Ultra 55 FEG SEM operating at Extra High Tension (EHT) of 5 kV. AFM topography images of PEDOT films on ITO slides were acquired using a P47 AFM (NT-MDT) equipped with a small scanner. Images were recorded in tapping mode in the air at room temperature (22−24 °C) using silicon micro cantilevers (OMCL-AC240TS-W2, Olympus). The set point ratio was adjusted to 0.75−0.8 (corresponding to "light" tapping) and the scan rate was set to 1 Hz. Imaging was carried out in different scan directions and at different scales to verify the consistency and robustness of the evaluated structures. Data were processed using the WSxM program.[41] XRD measurements of PEDOT films on ITO slides were performed on XRD diffractometer (TTRAX, Japan) equipped with Cu rotating anode.

Table 1. Electrochemical and Spectroelectrochemical Properties of PEDOT films Prepared Using Different Supporting Electrolytes and Solvents by Applying a Constant Potential of 1.15−1.20 V vs SCE (Fc/Fc$^+$ = 0.34 V under these conditions) and Passing a Charge of 50 mC

	E_{onset} (V)^a	$E_{1/2}$ (V)^b	$\lambda_{\max}$ (nm)^c	E_g (eV)^d
TBABF$_4$/PC	−0.34	−0.31	633 (188)	1.68 (737)
TBAClO$_4$/PC	−0.40	−0.32	633 (218)	1.68 (741)
LiBF$_4$/PC	−0.51	−0.39	635 (190)	1.66 (746)
LiClO$_4$/PC	−0.44	−0.31	635 (184)	1.68 (739)
TBABF$_4$/MeCN	−0.34	−0.28	621 (192)	1.68 (740)
TBAClO$_4$/MeCN	−0.45	−0.31	600 (206)	1.68 (740)
LiBF$_4$/MeCN	−0.58	−0.34	599 (215)	1.69 (732)
LiClO$_4$/MeCN	−0.59	−0.36	601 (210)	1.67 (744)

^{a} The onset of the oxidation potential calculated from the cyclic voltammetry curve of PEDOT film in a monomer-free electrolyte solution (see the Supporting Information for details). ^{b} $E_{1/2} = (E^{\mathrm{ox}}_{\mathrm{peak}} + E^{\mathrm{red}}_{\mathrm{peak}})/2$. ^{c} Wavelength of absorption peak maximum. The peak width at the half height (in nm) is given in parentheses. ^{d} The optical band gap calculated from the onset of the absorption peak. The values in nm are given in parentheses.

Results and Discussion

Electropolymerization. The electrochemical and optical properties of PEDOT films in four supporting electrolytes (TBAClO$_4$, TBABF$_4$, LiClO$_4$, and LiBF$_4$) and two solvents (PC and acetonitrile), prepared at a constant potential of 1.15−1.2 V (vs SCE) are summarized in Table 1. PC and acetonitrile were chosen since they are known to be the most common solvents for the electropolymerization of thiophenes, in general, and for the electrochemical preparation of electrochromic films based on conjugated polymers, in particular.[9,42] We observed that PEDOT films prepared in constant potential mode are of better quality and show better electrochromic properties than films prepared in dynamic CV mode (the morphological differences supporting this observation will be discussed below).

UV−Vis−NIR Spectroscopy. After polymerization, ITO-coated glass slides with PEDOT films were rinsed with acetonitrile and spectroelectrochemical measurements were performed in a UV−vis−NIR quartz cuvette.[39] Figure 1 shows absorption spectra in the vis-NIR region of PEDOT films measured at a constant potential of −1.0 V vs SCE. The films were prepared and measured using the conditions set out in Table 1. Clear differences between the absorption spectra were observed for PEDOT films prepared in PC versus acetonitrile. The absorption peaks of PEDOT films prepared in PC are red-shifted by 28 nm on average relative to the films prepared in acetonitrile (Figure 1a and Table 1). The maximal red-shift between the spectra of PEDOT films prepared in PC versus acetonitrile is 36 nm and was obtained for PEDOT films prepared with LiBF$_4$ as a supporting electrolyte. The absorption spectra of the PEDOT films prepared in PC show peaks with two well-defined shoulders originating from the vibronic structure, while films prepared in acetonitrile show no vibronic shoulders.[43] The spectra in PC are somewhat narrower than those of the films prepared in acetonitrile (the average half-peak width is 195 nm for the former compared to 206 nm for the

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(39) Although the measurements reported in this paper were performed in the same solvent as the electrochemical polymerization (PC or acetonitrile), in several cases, we also switched solvents by measuring the properties of films prepared in PC in acetonitrile and vice versa. We found that the physical (such as UV spectra) and electrochromic properties of PEDOT films depend significantly only on the solvent in which electropolymerization was performed and not on the solvent in which the measurements were performed.

(40) Each film type was prepared several times under the same conditions. Usually, some films were damaged or of somewhat lower quality and these films were discarded. Remaining films showed very uniform distribution of electrochromic parameters (within few percents) and the results reported are for the representative film, for which all data in Tables 1 and 2 were also obtained, and not necessarily for the best performing film.

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(42) It was suggested earlier that acetonitrile is a more efficient medium for producing adherent films of PEDOT and for the characterization of the resulting materials than PC and dichloromethane. See ref 9.

(43) The UV spectra and spectroelectrochemistry of PEDOT prepared in acetonitrile were reported several times in the literature, mostly by the Reynolds group (see refs 9 and 15) and by Sonmez, G.; Sonmez, H. B.; Chen, C. K. F.; Wudl, F. Adv. Mater. **2004**, *16*, 1905, and by others. The obtained UV spectrum is very similar to that reported here. The spectroelectrochemistry of PEDOT prepared in PC and measured in acetonitrile was also reported earlier (see ref 9 and Thomas, C. Ph.D. Thesis, University of Florida, Gainesville, FL, 2001). The reported UV spectrum shows observable shoulders, but they are not as clear as in our case.

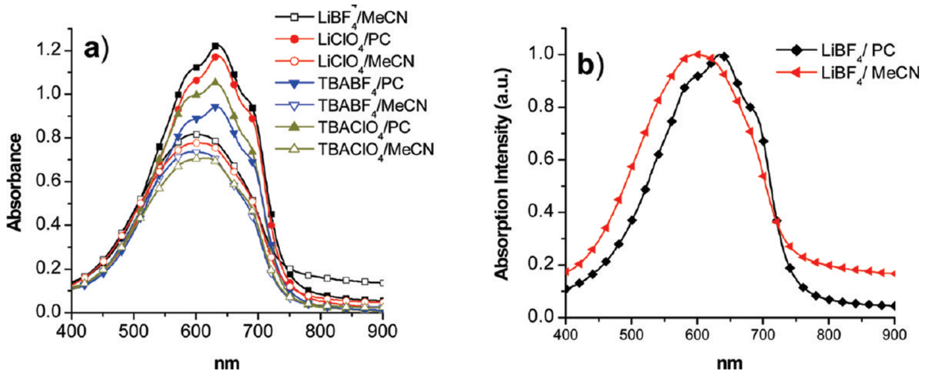

Figure 1. (a) vis−NIR spectra for PEDOT films prepared in different solvents and supporting electrolytes in the neutral state (−1.0 V vs SCE); (b) normalized vis−NIR spectra of PEDOT films prepared using $LiBF_4$/MeCN and $LiBF_4$/PC in the neutral state (−1.0 V vs SCE).

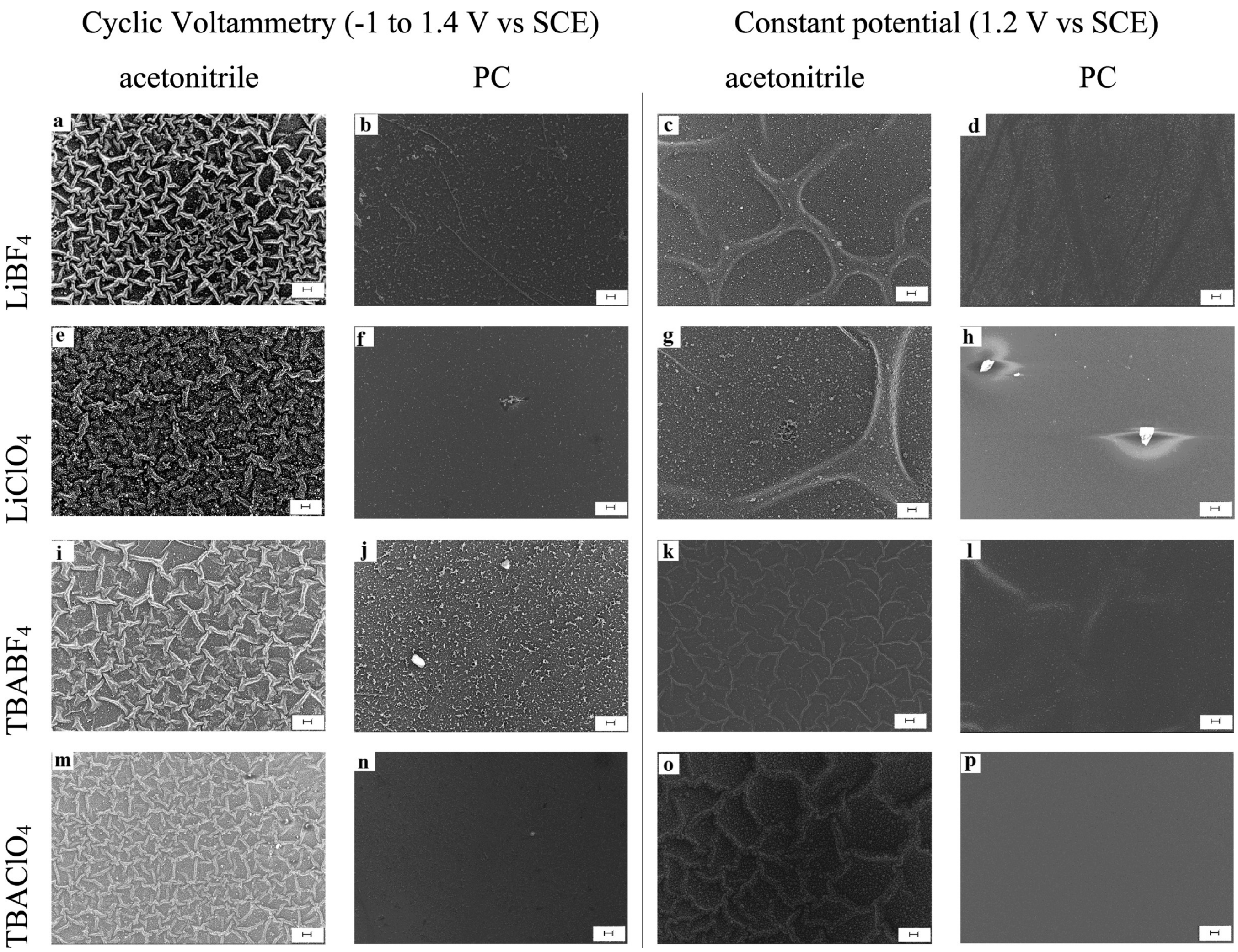

Figure 2. SEM images of eight pairs of PEDOT films on ITO electrode obtained using cyclic voltammetry (left two columns, a, b, e, f, i, j, m, n) and constant potential (right two columns, c, d, g, h, k, l, o, p) modes in acetonitrile (left image in each pair) and PC (right image in each pair). Supporting electrolytes are $LiBF_4$ (a−d); $LiClO_4$ (e−h); $TBABF_4$ (i−l); and $TBAClO_4$ (m−p). Magnification is ∼1000, scale bar is 10 μm, working distance is 3 mm, EHT is 5 kV.

latter).[39] The onset of the absorption spectrum, which is usually used to estimate optical band gap, is affected only slightly by changing the solvent and supporting electrolyte.[44]

Morphological Studies. *a. SEM*. To investigate correlations between the optical and structural properties of PEDOT films obtained under different conditions, their morphologies were studied using SEM. For SEM studies, we prepared the films using two solvents and four supporting

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(44) All the absorption spectra were obtained from the polymers prepared by passing 50 mC of charge. The absorption intensity of the films prepared in PC is consistently somewhat higher (on average by 30%) than that of the films prepared in acetonitrile (Figure 1a).

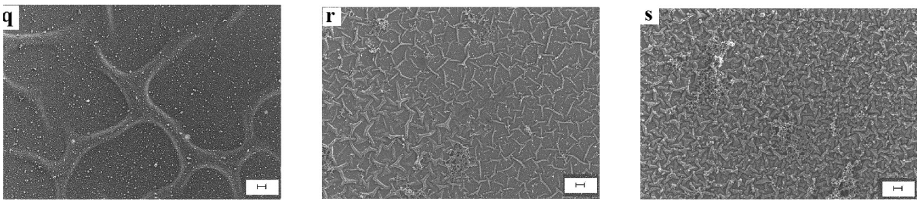

Figure 3. SEM images of PEDOT films prepared in $LiBF_4$/MeCN. Magnification is ∼1000, Scale bar is 10 μm. working distance is 3 mm, EHT is 5 kV. (q) Constant potential mode 1.2 V vs SCE; (r) cyclic voltammetry mode −1.0 to 1.4 V vs SCE; and (s) cyclic voltammetry mode (overoxidation) −1.0 to 1.6 V vs SCE.

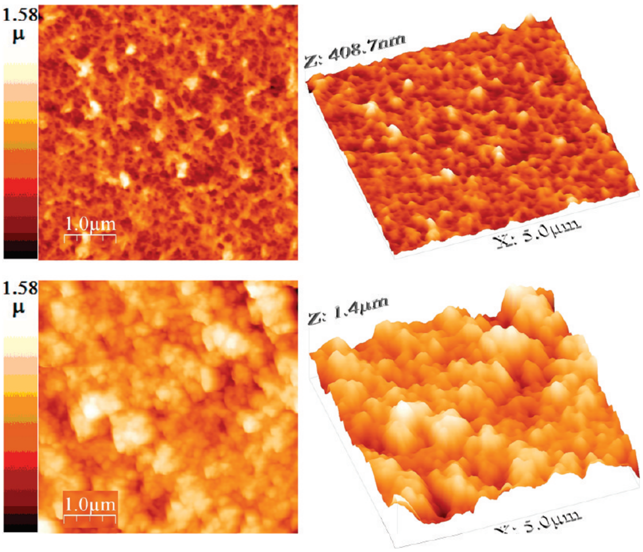

Figure 4. AFM images of PEDOT films prepared at a constant potential of 1.2 V vs SCE in PC (top) and acetonitrile (bottom) with $TBAClO_4$ as a supporting electrolyte. (Left) topography image, (right) 3D topography image.

electrolytes as set out in Table 1. SEM images at a magnification of ∼1000 (scale bar is 10 μm) are given in Figures 2 and 3. SEM images at a higher magnification (∼20000) are given in the Supporting Information. Both CV and constant potential modes were used to prepare the films.

We found that the supporting electrolyte has only a minor effect, while the solvent has a very clear and significant influence on the morphology of the polymer. While both preparation modes (CV and constant potential) show the same trends, the solvent/supporting electrolyte effect is better observed in films prepared by cyclic voltammetry. For instance, an examination of Figure 2 shows that films prepared in PC (images b, f, j, n for films prepared in CV mode, and images d, h, l, p for films prepared in constant potential mode) have smooth and flat morphology. On the other hand, films prepared in acetonitrile (images a, e, i, m for films prepared in CV mode, and images c, g, k, o for films prepared in constant potential mode) demonstrate a much more bumpy and rough structure. It is interesting to note that all films prepared in acetonitrile exhibit a star-shaped pattern, with the compactness of the "stars" depending on the polymerization method used (see below). Our morphological observations correlate well with the spectral data (Figure 1), showing that the effect of the solvent is major while the effect of the supporting electrolyte is minor and revealing that the films having a smoother structure (i.e., those obtained in PC) yield absorption spectra having vibronic shoulders and a longer λ_{max}.

The influence of the applied electrochemical method was also studied. Figure 3 shows SEM images of PEDOT films prepared in $LiBF_4$/MeCN under three different conditions: constant potential, cyclic voltammetry using the regular cyclic window (−1.0 to 1.4 V vs SCE), and cyclic voltammetry with overoxidation (−1.0 to 1.6 V vs SCE). It was found that films prepared using cyclic voltammetry have a rougher morphological structure than those prepared using a constant potential. Indeed, in film r, prepared by cyclic voltammetry, surface "stars" are much more closely packed that in film q prepared in constant potential mode (Figure 3). Overoxidation has a not very strong, but observable effect, leading to an even more star-crowded surface, as in the case of film s (Figure 3). The formation of rougher PEDOT films as a result of overoxidation was previously reported.[9,45] The appearance of these bumpy, micrometer-scale surface shapes may negatively affect the electrochromic properties of the films. These results of a morphological study using SEM correlate well with the electrochromic properties of the films (films prepared in constant potential mode show better electrochromic properties, see below).

The crystallinity of the films prepared in different solvents was investigated. We did not observe significant X-ray diffraction (XRD) signals in PEDOT films prepared either in acetonitrile or in PC.[46] This lack of crystallinity is consistent with the short switching times of the films prepared in this work (0.5−1.0 s, regardless of the solvent used), as crystalline films are known to have long switching times.[47]

b. AFM. To study film morphology at an even smaller scale, AFM studies were performed on PEDOT films prepared in acetonitrile and PC. The AFM data reveal distinct differences between films prepared in each solvent (Figure 4 and Supporting Information). PEDOT films prepared in PC are rough, although they clearly show a smoother surface with a lacelike morphology and homogeneous topography compared to samples prepared in acetonitrile, which have a very rough and hilly surface

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(45) Niu, L.; Kvarnström, C.; Fröberg, K.; Ivaska, A. *Synth. Met.* **2001**, *122*, 425.

(46) Overoxidation of EDOT in $TBAPF_6$/MeCN in a constant potential mode was reported to lead to crystalline PEDOT films. See ref 45.

(47) Xiong, S.; Phua, S. L.; Dunn, B. S.; Ma, J.; Lu, X. *Chem. Mater.* **2009**, *22*, 255–260.

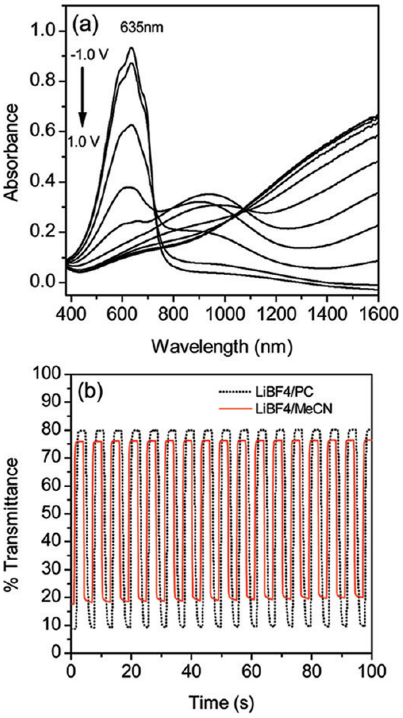

Figure 5. (a) Spectroelectrochemistry of a PEDOT film prepared using $LiBF_4$/PC on ITO-coated glass at applied potentials of −1.0 V to +1.0 V vs SCE at 0.2 V intervals using Ag/AgCl as a reference electrode; (b) percent transmittance of PEDOT films prepared in $LiBF_4$/PC (black dotted line) and $LiBF_4$/MeCN (red solid line) monitored at 635 and 621 nm, respectively, and switched between −1.0 and +1.0 V at 3 s intervals.

Table 2. Electrochromic Properties of PEDOT Films Measured at λ_{max} and Prepared Using Different Supporting Electrolytes and Solvents at a Constant Potential of 1.20 V vs SCE (Fc/Fc^+ = 0.34 V under these conditions) and by Passing a Charge of 50 mC[40]

	T_1%[a]	T_2%[b]	ΔT%	CE (cm^2/C)[c]
$TBABF_4$/PC	77.8	10.2	67.6	193
$TBAClO_4$/PC	78.6	12.1	66.5	132
$LiBF_4$/PC	79.9	9.2	70.7	171
$LiClO_4$/PC	76.2	7.9	68.3	186
$TBABF_4$/MeCN	77.3	20.7	56.6	144
$TBAClO_4$/MeCN	79.6	22.1	57.5	110
$LiBF_4$/MeCN	73.3	18.5	54.8	95
$LiClO_4$/MeCN	69.3	14.2	55.1	90

[a] The maximum transmittance of the film doped at +1.0 V vs SCE. [b] The minimum transmittance of the film dedoped at −1.0 V vs SCE. [c] Coloration efficiency.[26] See SI for Q_1 and Q_2 values. *A* is a working electrode area, 0.7 × 3.2 cm^2.

with significant topography drops. It is known that electrochemical polymerization results in relatively thick (hundreds of nanometers and even micrometer thick) films[9] and, indeed, the films we obtained are about 1 μm thick. Importantly, the roughness and height of the films prepared in acetonitrile is generally 3−4 times greater than that of films prepared in PC (whereas absorbance of the films prepared in acetonitrile is on average by 30% lower than that of the films prepared in PC,[44] see Figure 1a). For example, the average roughness (Figure 4) and maximal height of PEDOT film prepared in $TBAClO_4$/MeCN are 152.5 nm and 1.40 μm, respectively, while the corresponding values for film prepared in $TBAClO_4$/PC are 36.0 nm and 0.49 μm; (see the Supporting Information for similar data for other supporting electrolytes). Thus, AFM studies also confirm the correlation between surface smoothness and solvent used for polymerization.

Table 3. Optical and Electrochromic Data of PEDOT Films (Prepared and Measured in $LiBF_4$/PC) As a Function of Switching Percentage

% of full switch	ΔT%[a]	Q_d (mC/cm^2)[b]	ΔOD[c]	CE (cm^2/C)[d]
76	53	2.12	0.778	367
81	57	2.59	0.777	325
89	62	2.76	0.834	302
93	65	3.05	0.859	281
96	67	3.72	0.875	235
97	68	4.09	0.885	217
100	71	5.49	0.937	171

[a] $\Delta T\% = T_1\% - T_2\%$; values are obtained from the 7th switching step. [b] Injected charge per electrode area. [c] $\Delta OD = \log(T_1/T_2)$. [d] Coloration efficiency.[26]

Electrochromic Properties. The electrochromic characteristics,[12] such as contrast ratio (ΔT%) and coloration efficiency (CE), of PEDOT films prepared in different supporting electrolytes and solvents were studied.[40] Switching was performed at potentials stepped between −1.0 V and +1.0 V vs SCE at λ_{max} using a 3 s interval. A representative spectroelectrochemical graph for a PEDOT film is given in Figure 5a and a representative switching experiment performed on a PEDOT film is given in Figure 5b. All PEDOT films in the doped state (+1.0 V vs SCE) have a relatively high transmittance (T_1 is about 69.3−80%, Table 2) regardless of the supporting electrolyte and solvent used.[44] Indeed, PEDOT films are known to be good candidates for applications in transparent polymer electrodes[48] because of their high transparency in the doped state. Regarding the transmittance in the neutral state (−1.0 V vs SCE), PEDOT films prepared in PC show stronger absorption (T_2 = 8−12%, Table 2) than those prepared in acetonitrile (T_2 = 14−22%, Table 2). Consequently, the contrast ratios ($\Delta T = T_1 - T_2$) of PEDOT films prepared in PC are 9−16% higher than those prepared in acetonitrile using the same supporting electrolyte.[39]

The highest contrast ratio for a PEDOT film of 71% was obtained using $LiBF_4$/PC (Table 2 and Figure 5). This is significantly higher than the previously reported contrast ratio for a PEDOT film (54%), which was obtained in TBAPC/MeCN.[23] The enhancement of the contrast ratio of a PEDOT film by including an additional electrochromic element (viologen) into the polymer chain was reported.[49] However, the obtained contrast ratio (65%) is still lower than that obtained in this paper using PC as a solvent. The highest coloration efficiency of 193 cm^2/C (at full switch, 100%) was obtained for film prepared using $TBABF_4$/PC (Table 2). This coloration efficiency is similar to the previously reported values for PEDOT films (183 cm^2/C obtained in TBAPC/MeCN).[23] We note a clear correlation between the enhancement of electrochromic properties (which results from polymerization in PC), smoother morphology (as evidenced by SEM and

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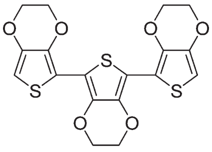
(48) Gurunathan, K.; Vadivel Murugan, A.; Marimuthu, R.; Mulik, U. P.; Amalnerkar, D. P. *Mater. Chem. Phys.* **1999**, *61*, 173.

(49) Ko, H. C.; Kang, M.; Moon, B.; Lee, H. *Adv. Mater.* **2004**, *19*, 1712.

AFM), the shape of the absorption band, and the identity of the solvent.[50]

Coloration efficiency can be increased by decreasing the switching window.[23] The coloration efficiency significantly increases and reaches a value of 367 cm^2/C (for PEDOT film prepared in LiBF$_4$/PC) when the switching voltage and, consequently, the contrast ratio, are decreased (Table 3). To the best of our knowledge, the coloration efficiency reported here is the highest reported for any electrochemically prepared PEDOT film. To test the long-term stability of PEDOT films prepared in PC, we selected the film prepared in LiBF$_4$/PC, because it has the highest contrast ratio. The PEDOT film was switched by stepping the potential between −1.0 and +0.6 V (this switching voltage produces the highest coloration efficiency of 367 cm^2/C with a contrast ratio of 53%) at an interval of 3 s in an electrochemical cell open to the air. After 6000 switching cycles, the contrast ratio was 37% and electroactivity remained 57%, showing that the stability of this film is similar to that of previously reported PEDOT films.[23]

Although the reason for the significant differences between the spectral, morphological, and electrochemical properties of PEDOT films prepared in PC compared to acetonitrile is unclear, we can speculate that differences in the solubility of EDOT oligomers produced at initial stages of electropolymerization in different solvents is responsible for such changes. Indeed, we have found that PC can dissolve short EDOT oligomers significantly better than acetonitrile. We tested the solubility of TER-EDOT[51] in both solvents and found that its solubility in PC (2×10^{-2} M) is about three times higher than in acetonitrile (7×10^{-3} M). In PC, large numbers of short oligomers that are produced during the initial stages of polymerization go into solution; therefore, the formation of relatively long polymeric chains on the electrode occurs and, consequently, a sharper UV spectrum, longer λ_{max}, and smoother films are observed. In acetonitrile, short oligomers are deposited on the electrode, leading to a high number of nucleation centers and terminated short oligomer chains compared to PC. This leads to more heterogeneous films from a chain length distribution point of view and results in a broader UV spectrum and shorter λ_{max} in acetonitrile. The high number of nucleation centers in acetonitrile results also in the very rough films observed in SEM and AFM. If indeed short oligomers are present in the films prepared in acetonitrile, this can explain the poorer electrochromic properties of these films, because short oligomers cannot be switched under the potentials used for switching long PEDOT chains. The band gap of the films obtained in both solvents is similar, because band gap is defined as the onset of the UV spectrum, which is governed by long polymeric chains. We also note that dielectric constant of PC (65) is significantly higher than that of acetonitrile (37). Higher dielectric constant can be important not only for oligomers solubility but also for polymerization conditions, since lower solution resistivity might lead to smoother films.



TER-EDOT

Conclusions

The effects of polymerization conditions, namely, the solvents, supporting electrolytes, and electropolymerization technique used, on the morphological structure and electrochromic properties of PEDOT films were systematically studied. Surprisingly, we found that the solvent has a major influence on the structural and electrochromic features of PEDOT films, the effect of the applied potential is quite significant, whereas the supporting electrolyte has only a moderate effect. Films prepared in propylene carbonate are significantly smoother than those prepared in acetonitrile. We suggest that differences in the solubilities of the EDOT oligomers produced during initial stages of electropolymerization in propylene carbonate and acetonitrile are responsible for this. We also found a correlation between the electrochromic features of a film and its morphological structure: a smoother and flatter morphology results in the film having better electrochromic properties. In addition, PEDOT films prepared in LiBF$_4$/PC have an exceptionally high contrast ratio (71%) and transparency in the doped state (80%), whereas PEDOT films prepared in PC/TBABF$_4$ reach a coloration efficiency of 193 cm^2/C at a full switch (100%).

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Supporting Information Available: Detailed electrochemical data, SEM, and AFM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(50) The switching time is similar to previously reported data for electropolymerized PEDOT films (see ref 10a) (below 1 s) and it does not depend on the solvent used.

(51) TER-EDOT was synthesized using Stille coupling of 2,5-dibromo-EDOT with 2-tri(*n*-butyltin)EDOT and the spectral data of obtained TER-EDOT are identical to those reported in: Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.