



## Variable-color poly(3,4-propylenedioxythiophene) electrochromics from precursor polymers

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### ABSTRACT

We have developed two approaches to processable precursors to conjugated polymers: main-chain and side-chain. Upon oxidative conversion to the conjugated polymer, a main-chain precursor yielded a nearly perfect spectral match, an identical  $\lambda_{\text{max}}$ , and an equivalent band gap to that of electrodeposited chromophore, resulting in a color match. This precursor method has the potential to incorporate any chromophore and achieve spectral and color matching with relative ease, as opposed to extensive synthetic monomer design. We describe the synthesis and characterization of a new side-chain and two new main-chain precursor polymers, each of which contains a derivative of 3,4-propylenedioxythiophene, ProDOT-Me<sub>2</sub>. The side-chain precursor tethers one ProDOT-Me<sub>2</sub> molecule to a poly(norbornene) backbone; the main-chain systems are perfectly alternating copolymers of ProDOT-Me<sub>2</sub>, one with dimethylsilane and one with tetramethyldisiloxane. Electronic and optical properties for these converted precursors were described and compared to electrodeposited PProDOT-Me<sub>2</sub>.

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### 1. Introduction

ProDOT-Me<sub>2</sub> continues to be an exciting molecule for electrochromics, due in part to its high contrast and blue to (essentially) colorless transition. Conjugated and conducting polymer processing constraints have led to the search for methods other than electrodeposition or bulk chemical polymerizations for creating and patterning these materials. Various methods have been explored which solve the processing issue [1–9], including methods developed by our group such as the main-chain precursor polymer approach [10] and the side-chain precursor polymer approach [11,12]. Side-chain precursors have the advantage of being made photopatternable, while main-chain precursors are melt-processable, as we have demonstrated [13,14]. The precursor polymer technique is an effective method for preparing films and nanofiber mats of conducting polymers from processable precursor polymers. Various pre- and post-derivatizations have been performed in the hopes of imparting processability as well as color variation, and hybrid materials have also been investigated [15–23]. These precursor-based processing methods involve an oxidative conversion process that can be accomplished in the solid state via chemical or electrochemical means. A soluble, insulating precursor

polymer can be patterned in any number of ways (spin coating, spray coating, ink-jetting, melt-processing, drop-casting, e-spinning, etc.); after which, oxidative conditions will cause a conversion to occur wherein the electroactive species in the precursor polymers couple and form an insoluble, conjugated polymer, which is electrochromic.

These precursors are versatile materials, allowing for the incorporation of many different thiophenes, including 3,4-ethylenedioxythiophene (EDOT), as well as other aromatic heterocycles or fused ring systems. The achievement herein is the spectral and color match to PProDOT-Me<sub>2</sub> that was accomplished by the conversion of a precursor polymer. Polymer chain mobility, crosslinking effects, and leeching into electrolyte during the conversion process are all factors which dictate the effective conjugation length and  $\pi$ -orbital overlap, causing the observed variable-color systems.

The processing issue has led to many different approaches, each of which has their own effect on the final color of the polymer obtained. These effects make it difficult to predict the color of the final electrochromic system. Our system eliminates the uncertainty associated with synthetic monomer design. We are able to create a simply prepared precursor polymer making use of any number of aromatic, electroactive monomers. The monomers, whose colorimetric properties are well known through electrochemical polymerization, can then be processed and subsequently converted. The conjugated, electrochromic product of this process will yield a material whose colorimetric properties are the same as that of the

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electrodeposited polymer. This shows the remarkable versatility of this method, lending itself to the development of a full library of colors. Such development could be a necessary component for the realization of full-color electrochromic displays.

## 2. Experimental

### 2.1. Materials

Acetonitrile (ACN) and dichloromethane (DCM) were purchased from Thermo-Fisher and distilled over calcium hydride to dry before using. Xylene and toluene were purchased from Thermo-Fisher and dried over sodium prior to use. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>), lithium trifluoromethane sulfonate (LITRIF), propylene carbonate (PC), polyethylene glycol diacrylate (PEG-DA), and dimethoxyphenylacetophenone (DMPAP) were purchased from Sigma–Aldrich and used as received. Indium-doped Tin Oxide (ITO)/glass cuvette slides (0.7 × 7 × 55 mm, 1.5" × 2", and 3 × 3 inch,  $R_s = 8\text{--}12\ \Omega$ , unpolished float glass SiO<sub>2</sub> passivated) were purchased from Delta Technologies and cleaned by sonication in acetone prior to use. Polyethylene terephthalate (PET)–ITO substrates were purchased from CP Films, also cleaned by sonication in acetone prior to use. Anhydrous magnesium sulfate, *N*-bromo succinimide (NBS), 1-bromooctane, *N,N*-dimethyl formamide, thionyl chloride, tetrahydrofuran (THF), petroleum ether, chloroform, hexane, dodecylbenzene sulfonic acid, 2-(hydroxymethyl)-2-methylpropane-1,3-diol, and triethylamine were purchased from Thermo-Fisher and used as received. 2.5 M *n*-Butyl lithium in hexanes was purchased from Sigma–Aldrich and titrated for accuracy prior to use. 2,2-Dimethylpropane-1,3-diol, 5-norbornene-2-carboxylic acid, and 5-norbornene-2-methanol (mixtures of endo and exo for both) were each purchased from Sigma–Aldrich and used as received. Grubbs' Generation I Catalyst was purchased from STREM Chemicals and stored in a glove box. Deuterated chloroform was purchased from Cambridge Isotope Laboratories and used as received. 3,4-Dimethoxythiophene was synthesized according to literature procedure [24]. Silica gel was purchased from Sorbent Technologies and was used as received. Dimethyldichlorosilane and tetramethyldichlorodisiloxane were purchased from Gelest, Inc. and distilled prior to use (stored in desiccator).

### 2.2. Instrumental

Spectroelectrochemical measurements were taken using a Varian Cary 5000 Spectrophotometer with a 150 mm Integrating Sphere DRA accessory. Colorimetric data were calculated using the accompanying Varian software using CIE 1976 Lu'v' color coordinates, a 10° observer, and a D65 illuminant. Electrochemical experiments were carried out with CH Instruments 660A, 400 and 400A potentiostats. Thermogravimetric analysis (TGA) was performed on a TGA Q-500 using both inert and oxygen atmospheres and Differential Scanning Calorimetry (DSC) was performed on a DSC Q-100. The TGA was run by first heating to 120 °C to drive off solvent, cooling back to 50 °C and then heating to 600 °C at 20 °C/min. DSC was carried out at 10 °C/min. Gel Permeation Chromatography was carried out on a Viscotek GPC MAX; using THF, samples of these polymers were passed through 0.45 μm filters and run through a standard GPC column with polystyrene standard calibration. Nuclear Magnetic Resonance (NMR) spectroscopy was carried out on a Bruker DMX500 instrument analyzed with XWINNMR software. Film thicknesses were obtained by using a Veeco Dektak mechanical profilometer. Electron microscopy was performed using an AMRAY 1810 SEM and IXRF Systems Inc 500 Digital Processing. Films with similar film thicknesses (within 25 nm of one another) were prepared on ITO/glass cuvette slides

via spray casting for imaging, except for the control material which was electrodeposited. Films made on Pt button working electrodes were drop cast.

### 2.3. Electrochemistry

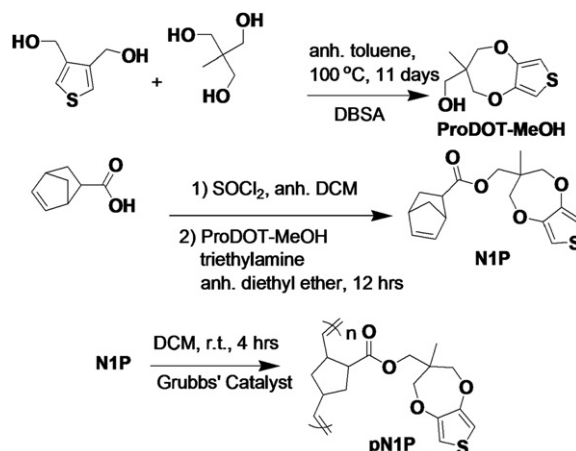
Switching speed and basic CV studies of the polymers are performed on a platinum button electrode (0.2 cm diameter) using a platinum flag counter electrode (1 cm<sup>2</sup>), a non-aqueous Ag/Ag<sup>+</sup> reference electrode, calibrated against the ferrocene/ferrocenium couple to be 0.455 V vs. NHE. The electrolyte bath was 0.1 M LITRIF in acetonitrile. The buttons were exposed by drop-casting to precursor polymer solutions in DCM of each polymer and allowed to dry in air before submersion in the three-electrode cell. The scan rate dependency of each converted polymer thin film adhered to the electrode surface follows the modified Randles–Sevcik equation ( $i_p = n^2 F^2 A \Gamma_s \nu / 4RT$ ; where  $i_p$  is the peak current,  $n$  is the number of moles,  $F$  is Faraday's constant,  $A$  is the electrode area,  $\Gamma_s$  is the total surface concentration of the film,  $\nu$  is the scan rate,  $R$  is the gas constant, and  $T$  is the temperature), such that the current response grew linearly with a linear increase in scan rate in all cases.

Spectroelectrochemistry was carried out on films of the precursors which were spray coated for the same amount of time from DCM solutions of the same concentration onto ITO/glass cuvette slides and annealed at 100 °C for 20 min before conversion (using the same electrochemical setup and reference as described for the button electrode conversions).

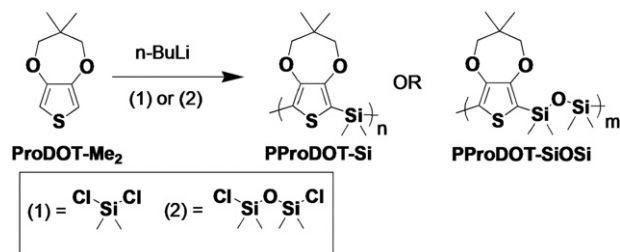
## 3. Results and discussion

### 3.1. Polymer synthesis and properties

New monomers are constantly being developed and explored in order to controllably tune the band gap, color transitions, and polymer properties of the resultant materials. The precursor polymers herein involve the use of ProDOT-Me<sub>2</sub> moieties. ProDOT-Me<sub>2</sub>-containing precursors are a step towards processability from a monomer that is often polymerized via electro-oxidation to generate a high contrast blue to colorless electrochromic. The synthesis of a ProDOT derivative with an alcohol substituent allowed for the attachment of a single electroactive fused heterocycle to the norbornene, which undergoes ROMP to yield the precursor abbreviated pN1P (Scheme 1). Further, the synthesis of the silane and siloxane precursors, alternating copolymers of a solubilizing spacer and ProDOT-Me<sub>2</sub>, appears in Scheme 2. The



Scheme 1. Synthetic scheme for the preparation of pN1P.



**Scheme 2.** Synthetic scheme for the preparation of PProDOT-Si and PProDOT-SiOSi.

simplicity of the main-chain syntheses is evident. Synthetic details are available in the [Supporting information](#).

The precursor polymers were soluble in traditional organic solvents, like toluene, THF, DMF, and DCM. Using polystyrene calibration standards, the  $M_n$ s for pN1P, PProDOT-Si, and PProDOT-SiOSi were determined to be 65,413 (PDI = 1.11; DP = 195), 2100 (PDI = 1.35; DP = 9), and 8800 (PDI = 1.22; DP = 31) respectively. DSC was carried out and it revealed the following glass transition temperatures ( $T_g$ s) for the precursors: pN1P = 65 °C; PProDOT-Si = 61 °C; PProDOT-SiOSi = 26 °C. TGA was performed on pN1P in  $N_2$  and in  $O_2$  atmospheres, to observe decomposition; under both atmospheres, the polymer was found to have an onset of degradation occur at 375 °C and 50% mass loss occurred at 415 °C. Complete degradation occurred only under  $O_2$  atmosphere, the polymer having reached essentially no mass remaining by 475 °C. Degradation onset temperatures for the silane and the siloxane are 275 °C and 347 °C, respectively. Note that the temperatures for 50% mass loss for the silane and siloxane are 375 °C and 451 °C, respectively.

### 3.2. Electronic and optical properties

A myriad of new materials, varying in color from green to black, have been developed and have been made processable [25–32]. Work with these chromophores in typical electrochromic device architectures has also been important to our group with the recent incorporation of poly(thieno[3,4-*b*]thiophene) as an ion storage layer [33]. It is this desire to easily prepare processable electrochromic materials that makes the precursors herein of value. We have the ability to simply incorporate a chromophore of the desired color into a soluble, processable precursor and subsequently achieve the same color from conversion of this material as is achieved with electrodeposition.

For the side-chain approach, oxidation causes crosslinking of the pendant units. In the main-chain approach, cleavage of the silane or siloxane unit (electrochemically or chemically) results in the coupling of the aromatic units. It has been found that, though these three precursors have the same chromophore, the siloxane precursor yielded the closest color match to electrodeposited ProDOT-Me<sub>2</sub>. The crosslinking in the pendant-approach, coupled with the restrictions of the norbornene backbone itself, does not lend itself towards achieving a saturation of properties for its ProDOT-Me<sub>2</sub> moiety. Indeed, as a control, electrochemical polymerizations of N1P from solution (the monomer prior to the precursor polymer) result in a material with color transitions similar to that of other PProDOTs with bulky substituents, which are typically blue to colorless [34]. Further, bisTMS-ProDOT-Me<sub>2</sub> monomer was also synthesized and electropolymerized from solution, yielding a material that matched the properties of PProDOT-Me<sub>2</sub>. This means that it is either the extent of crosslinking or a constrained geometry of the backbone that limits linear conjugation and  $\pi$ -orbital overlap.

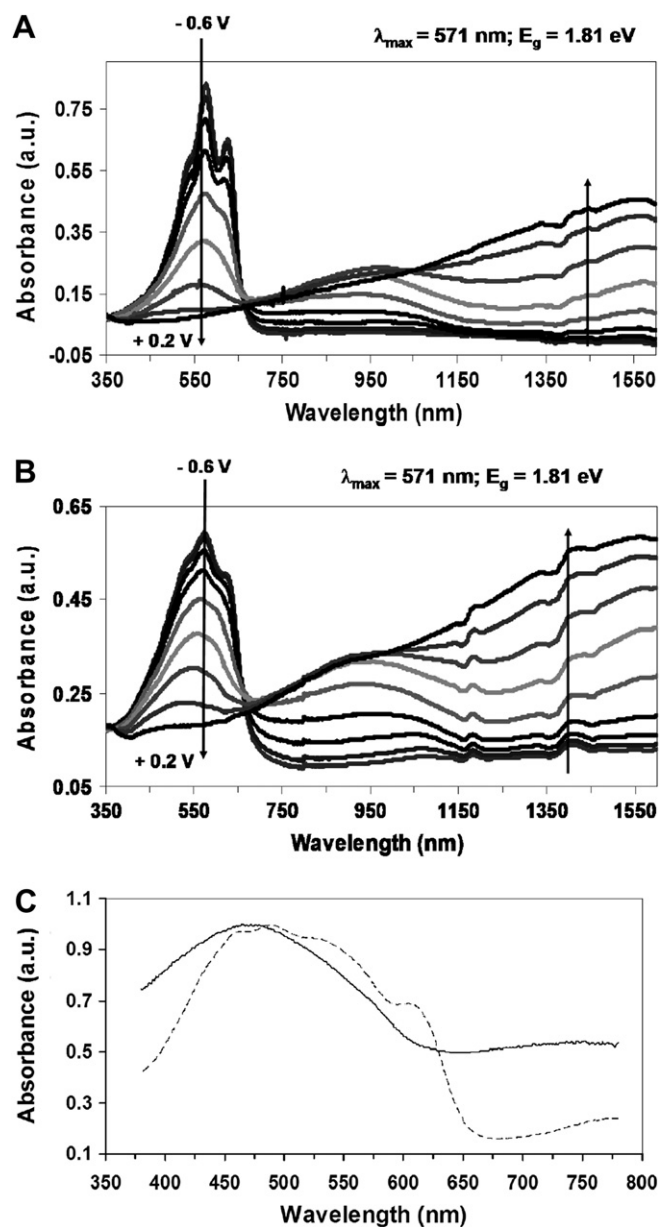
These precursors were used for *in situ* conversion, a process recently developed for the preparation of solid state devices [35]. Under these conditions, where an electrolyte bath is not necessary, we achieved the same color match to PProDOT-Me<sub>2</sub> with the silane as for the siloxane. The reason for this is the leeching of the monomer during the conversion process, as well as the escape of oligomeric precursor into solution prior to the application of potential. This was spectroscopically determined by examining the electrolyte bath both pre- and post-immersion and pre- and post-conversion. The lower molecular weight system, PProDOT-Si, was not as amenable to solution conversions as the other precursors and thus resulted in a system with less conjugation.

Chemical oxidants, such as ferric chloride (FeCl<sub>3</sub>), may be applied to films on non-conductive substrates in order to achieve conversion. However, for most characterization methods, including optical studies, electrochemical conversion is preferred. Cyclic voltammetry (CV) is employed to ascertain the electronic properties of the materials. This method showed the oxidation potential necessary for the conversion of precursor to electrochromic, as well as the redox processes of the resultant polymer. The thin film on the electrode was also probed for its adherence to theoretical current responses by cyclic voltammetric scan rate studies, which showed a linear increase of current response to increases in scan rate.

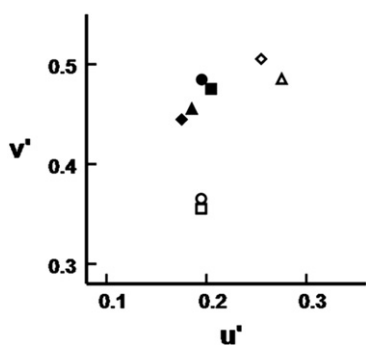
For pN1P, the CVs show an onset for precursor polymer oxidation, and thus conversion to conjugated polymer, at 0.88 V and a sharp peak at 1.07 V. The polymer had observed redox-active peaks at 0.45 V (oxidation) and 0.30 V (reduction). The redox window for pN1P is from 0.0 V to 0.8 V. For PProDOT-Si the conversion onset is at 0.8 V, with a pre-peak at 0.94 V and a main peak at 1.3 V. The operating window for PProDOT-Si is from –0.445 V to 0.656 V with redox peaks appearing at 0.242 V and 0.411 V for oxidation and at 0.225 V and –0.159 V for reduction. For PProDOT-SiOSi the onset for conversion occurs at 0.953 V, with a peak appearing at 1.330 V. The converted polymer had redox-active peaks at –0.016 V and –0.325 V. The redox window is from –0.65 V to 0.60 V. For ProDOT-Me<sub>2</sub>, the polymerization potential is 1.3 V with an onset for polymerization at 1.09 V. The operational voltage window for the polymer, PProDOT-Me<sub>2</sub> is –0.52 V to 0.50 V with redox-active peaks at 0.08 V and –0.134 V. The higher voltages necessary for redox switching of pN1P and PProDOT-Si indicate materials which are harder to oxidize. In other words, their respective conjugation lengths are shorter than that of PProDOT-Me<sub>2</sub> and PProDOT-SiOSi. The converted PProDOT-SiOSi has similar electronic properties as compared to electrodeposited PProDOT-Me<sub>2</sub>, offering further evidence that the resultant polymers match each other. All CVs for growth, conversion, and polymer redox appear in the [Supporting information](#).

In order to obtain the color properties of these materials, spectroelectrochemical measurements were taken for electrochemically converted films of each precursor, as well as electrochemically grown films of the pristine chromophore, ProDOT-Me<sub>2</sub>. Fig. 1 illustrates the full spectroelectrochemistry for PProDOT-Me<sub>2</sub> and converted PProDOT-SiOSi, at iterative voltages. The absorption maximum is the same, as is the band gap ( $E_g = 1.81$  eV). This is a clear illustration of the overlapping properties for PProDOT-SiOSi as compared to PProDOT-Me<sub>2</sub>. The same experiments were performed on PProDOT-Si and pN1P, however they did not yield spectral matches to electrochemically generated PProDOT-Me<sub>2</sub>. They exhibited reddish to bluish color transitions, consistent with their different absorbance maxima (Fig. 1C).

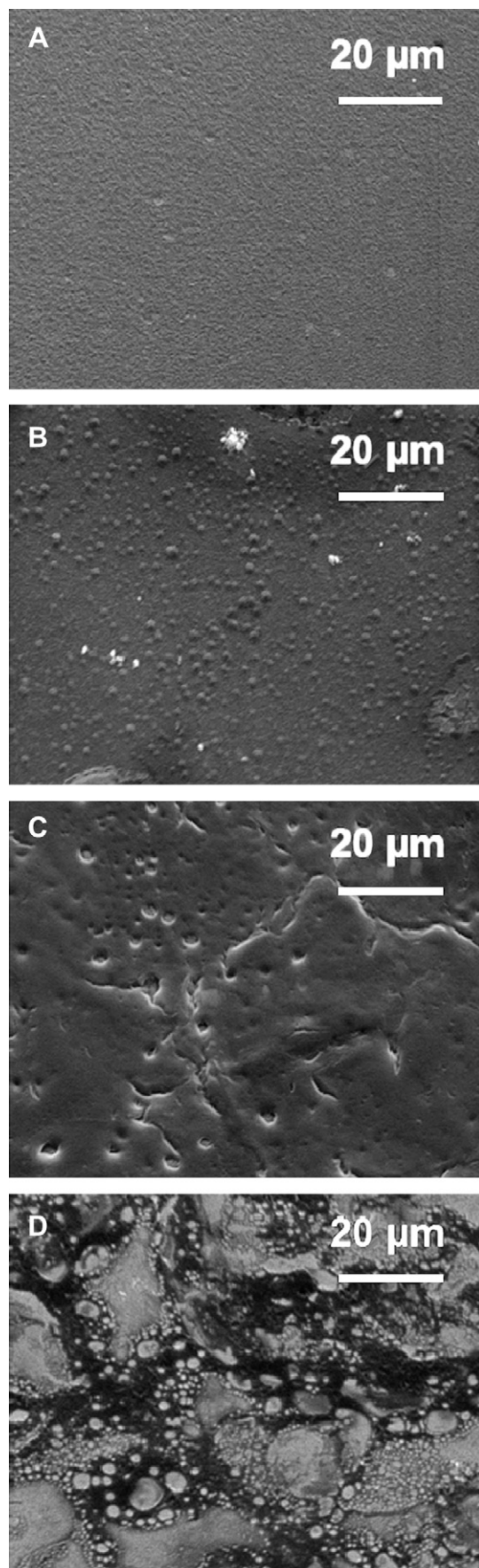
Color coordinates were calculated for all films. Fig. 2 contains the color coordinates for the siloxane precursor and for electrodeposited PProDOT-Me<sub>2</sub> in their oxidized and neutral states. Notably, a spectral and colorimetric match to that of PProDOT-Me<sub>2</sub> is obtained for converted films of PProDOT-SiOSi. The small



**Fig. 1.** Spectroelectrochemistry in the UV–Vis–NIR for PProDOT-Me<sub>2</sub> (A) and converted PProDOT-SiOSi (B), showing a close spectral match of the converted precursor to the pristine chromophore. Also, spectral overlay in the visible spectrum (C) for the neutral states of PProDOT-Si (dashed line) and pN1P (solid line).



**Fig. 2.** CIE Lu'v' color coordinates for the chromophores. PProDOT-Me<sub>2</sub> (square), PProDOT-SiOSi (circle), PProDOT-Si (triangle), and pN1P (diamond). Empty represents the neutral states and filled represents the oxidized states of each polymer.



**Fig. 3.** SEM images of (A) PProDOT-Me<sub>2</sub>, (B) PProDOT-SiOSi, (C) PProDOT-Si, and (D) pN1P.



difference in the color coordinate values between PProDOT-Me<sub>2</sub> and converted PProDOT-SiOSi is attributed to the broadness of the spectrum for the latter. Both materials display a deep purple-blue color in their neutral state and go to a transmissive, sky-blue in the oxidized state. The color transitions for converted pN1P and PProDOT-Si are from reddish neutral states to light blue oxidized states.

### 3.3. Film morphology and switching speed

The nature of the conversion process and the crosslinking process of the precursor polymers differs significantly from electrodeposition, which is a nucleation and growth mechanism. Norbornene precursors rely on the crosslinking of their pendant units upon oxidation, whereas the silane and siloxane systems involve the cleavage of the spacer units. However, the coupling of the aromatic units can occur both intra-chain and inter-chain. For each precursor, a film is made prior to conversion, whereas electrodeposition occurs from monomer solution. These differences in the mechanism of film formation result in a multitude of film morphologies and roughnesses. SEM images were taken for films of each of the four systems, and these appear in Fig. 3. Notably, the similarity in film morphology of PProDOT-Me<sub>2</sub> with both PProDOT-Si and PProDOT-SiOSi. PProDOT-Me<sub>2</sub> is overall rough, with many small features across its surface. PProDOT-SiOSi is similarly rough, with somewhat larger spherical features. PProDOT-Si appears much less uniform, however, and exhibits porosity and cracking. Finally, pN1P exhibits an irregular topology as a result of its crosslinking nature and norbornene backbone. Many nanoscale features appear in the film and they are severely scattered across the surface.

The switching speeds for each material were evaluated, as well, representing the same film area and approximately the same film thicknesses. Thickness values averaged  $300 \pm 25$  nm. PProDOT-Me<sub>2</sub> switches completely within 100 ms, whereas PProDOT-SiOSi switches in 200 ms, PProDOT-Si switches in 250 ms, and pN1P switches in just over 700 ms. The similarity in switching properties between electrodeposited and converted main-chain precursors is expected. The relative slowness of the pendant system is also expected as a result of the crosslinking nature of the conversion and the presence of the norbornene backbone itself, causing diffusion effects within the film. Optical memory for all of these systems in solution persists for over 30 min, by absorbance measurements (less than 1% loss of absorbance over this time period).

## 4. Conclusion

We have demonstrated the inclusion of ProDOT moieties into soluble precursor polymers which easily undergo solid state oxidative conversion to form conjugated, electrochromic polymers. It has been shown that the use of a siloxane precursor polymer achieves comparable spectroelectrochemistry and contrast values as that of pristine, electrodeposited ProDOT-Me<sub>2</sub>. The ease of these systems to incorporate potentially any other chromophore, and thereby achieve a predictable color match when using a processable precursor would make this method broadly applicable. The precursors have been processed via electrospinning and spray coating and could easily be translated into ink-jetting, spin casting, or any other conventional solution-based technique. Ease of processing and conversion makes the assembly of ECDs even more facile. Also, copolymerization can be used to achieve variations of the colored states observed. The versatility of the precursor method in that regard is as attractive as its processing properties. The conversion process of precursors, such as those discussed herein, offers the benefit of being converted and switched in the medium in which they will eventually be used, possibly resulting in an

advantage over materials which require a “breaking in” period for counterion shuttling.

## Acknowledgement

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## Appendix. Supporting information

Cyclic voltammetry and UV–Vis spectra for each of the four systems described above, as well as synthesis information for the same, are available. The supplementary data associated with this article can be found, in the on-line version, at [doi:10.1016/j.polymer.2009.12.015](https://doi.org/10.1016/j.polymer.2009.12.015).

## References

- [1] (a) Bordeau M, Frebault F, Gobet M, Picard J-P. *Eur J Org Chem* 2006;18:4147–54; (b) Palmaerts A, Lutsen L, Cleij TJ, Vanderzande D, Pivrikas A, Neugebauer H, et al. *Polymer* 2009;50(21):5007–15.
- [2] Jeffries-El M, Sauve G, McCullough RD. *Macromolecules* 2005;38(25):10346–52.
- [3] *Eur. Patent No. 440957*; 1991.
- [4] Reeves BD, Grenier CRG, Argun AA, Cirpan A, McCarley TD, Reynolds JR. *Macromolecules* 2004;37:7559–69.
- [5] Zong Z, Reynolds JR. *J Org Chem* 2001;66:6873–82.
- [6] Walczak RM, Leonard JK, Reynolds JR. *Macromolecules* 2008;41:691–700.
- [7] Witker D, Reynolds JR. *Macromolecules* 2005;38:7636–44.
- [8] Cirpan A, Argun AA, Grenier CRG, Reeves BD, Reynolds JR. *J Mater Chem* 2003;13:2422–8.
- [9] Lee B, Seshadri V, Palko H, Sotzing GA. *Adv Mater* 2005;17:1792–5.
- [10] Bokria JG, Kumar A, Seshadri V, Tran A, Sotzing GA. *Adv Mater* 2008;20(6):1175–8.
- [11] Jang S-Y, Sotzing GA, Marquez M. *Macromolecules* 2004;37(12):4351–9.
- [12] Jang S-Y, Sotzing GA, Marquez M. *Macromolecules* 2002;35(19):7293–300.
- [13] (a) Asemota CI, Kumar A, Sotzing GA. *MRS symposium proceedings*; 2007 [948E: Paper #: 0948-B05-15]; (b) Choi J, Ling GH, Shaw MT, Sotzing GA. *Polym Prepr* 2007;48(1):97–8.
- [14] Kumar A, Jang S-Y, Padilla J, Otero TF, Sotzing GA. *Polymer* 2008;49(17):3686–92.
- [15] Bhandari S, Deepa M, Srivastava AK, Kant R, J Mater Chem 2009;19(16):2334–48.
- [16] Lim B, Nah Y-C, Hwang J-T, Ghim J, Vak D, Yun J-M, et al. *J Mater Chem* 2009;19(16):2380–5.
- [17] Sharmoukh W, Ko KC, Ko JH, Nam HJ, Jung D-Y, Noh C, et al. *J Mater Chem* 2008;18(37):4408–13.
- [18] Shim GH, Han MG, Sharp-Norton JC, Creager SE, Foulger SH. *J Mater Chem* 2008;18(5):594–601.
- [19] Small WR, Masdarolomoor F, Wallace GG, Panhuis M. *J Mater Chem* 2007;17(41):4359–61.
- [20] Chang C-W, Liou G-S, Hsiao S-H. *J Mater Chem* 2007;17(10):1007–15.
- [21] Berridge R, Wright SP, Skabara PJ, Dyer A, Steckler T, Argun AA, et al. *J Mater Chem* 2007;17(3):225–31.
- [22] Walczak RM, Cowart JS, Reynolds JR. *J Mater Chem* 2007;17(3):254–60.
- [23] Mishra SP, Krishnamoorthy K, Sahoo R, Kumar A. *J Mater Chem* 2006;16(32):3297–304.
- [24] von Kieseritzky F, Allared F, Dahlstedt E, Hellberg J. *Tetrahedron Lett* 2004;45:6049–50.
- [25] (a) Aydemir K, Tarkuc S, Durmus A, Gunbas GE, Toppare L. *Polymer* 2008;49(8):2029–32; (b) Tarkuc S, Udm Y, Toppare L. *Polymer* 2009;50(15):3458–64; (c) Song S, Jin Y, Kim J, Park SH, Kim SH, Lee K, et al. *Polymer* 2008;49(26):5643–9; (d) Yildiz HB, Sahin E, Cirpan A, Toppare L, Yagci Y. *Polym Int* 2007;56(5):674–8.
- [26] (a) Unur E, Jung JH, Mortimer RJ, Reynolds JR. *Chem Mater* 2008;20(6):2328–34; (b) Tehrani P, Hennerdal LO, Dyer AL, Reynolds JR, Berggren M. *J Mater Chem* 2009;19:1799–802.
- [27] Andersson P, Forchheimer R, Tehrani P, Berggren M. *Adv Funct Mater* 2007;17:3074–82.
- [28] Beaujuge PM, Ellinger S, Reynolds JR. *Nat Mater* 2008;7:795–9.
- [29] Gunbas GE, Durmus A, Toppare L. *Adv Mater* 2008;20:691–5.
- [30] Durmus A, Gunbas GE, Toppare L. *Chem Mater* 2007;19(25):6247–51.
- [31] Beaujuge PM, Ellinger S, Reynolds JR. *Adv Mater* 2008;20:2772–6.
- [32] Dyer AL, Grenier CRG, Reynolds JR. *Adv Funct Mater* 2007;17:1480–6.
- [33] Invernale MA, Seshadri V, Mamangun DMD, Ding Y, Filloramo J, Sotzing GA. *Chem Mater* 2009;21(14):3332–6.
- [34] Padilla J, Seshadri V, Filloramo J, Mino WK, Mishra SP, Radmard B, et al. *Synth Met* 2007;157(6–7):261–8.
- [35] Invernale MA, Ding Y, Mamangun DMD, Yavuz MS, Sotzing GA. *Adv Mater* 2009;21:1–4.