Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

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Block Copolymer Supramolecular Assembly using a Precursor to a Novel Conjugated Polymer

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Electropolymerization

bisEDOT was electropolymerized on a Pt electrode from a 5 mM monomer solution in 0.1M $TBAPF_6$/ACN. The bisEDOT monomer's peak anodic oxidation potential (E_{pa}) was observed at 0.71 V and was part of an irreversible cyclic voltammogram. This E_{pa} is 0.29 V lower than that of EDOT (1.0 V vs. Ag/Ag^+).[1] The lower oxidation potential of bisEDOT compared to EDOT is due to the extended conjugation through the 1,6-methano[10]annulene ring. The irreversible CV is in contrast with what we have observed for other 1,6-methano[10]annulene-containing monomers investigated previously that have provided much more stable oxidation intermediates. bisEDOT grew much more efficiently than the other 1,6-methano[10]annulene containing polymers we have reported previously.[2, 3] The efficient polymerization is evident in the bisEDOT growth profile (Figure 1a) as well as the thickness of the film formed on the working electrode. The irreversibility of the monomer CV may be a sign of how quickly the radical-cation formed reacts with another bisEDOT molecule.

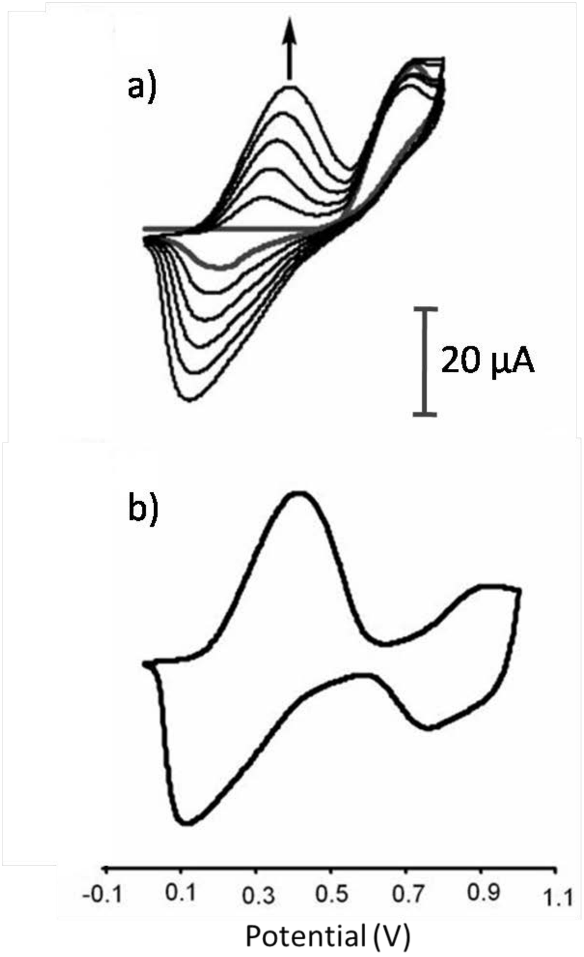

Figure 1. Polymer growth profile of bisEDOT obtained

from 5 mM monomer solutions in 0.1 M TBAPF$_6$/DCM using a 1.6 mm Pt button working electrode, coiled Pt wire as the counter electrode and a silver wire submersed in 0.01 M AgNO$_3$ as the reference electrode. Scan rate = 100 mV/s and grey curve = monomer CV (a).Polymer CV of poly(bisEDOT) obtained in 0.1 M TBAPF$_6$ in DCM using the polymer-coated Pt button electrode as the working electrode(b). Other conditions for (b) are the same as the polymer growth profile.

Polymer Electrochemistry

The polymer-coated electrode was rinsed with monomer-free electrolyte and the CV of the polymer was then recorded in 0.1 M TBAPF$_6$ in DCM. The CV obtained for poly(bisEDOT) was most unexpected as it possessed what appeared to be two separate and reversible oxidation processes. The oxidation potential of the first was observed at 0.35 V and that of the other at 0.87 V (Figure 1b). The intensity of the peak current varied linearly with the scan rate when cyclic voltammograms were recorded by scanning between 0.0 V and 1.0 V. A stability check was performed by scanning between 0 and 1.0 V for 30 cycles at which point the peak current of the CV decreased minimally and the features remained the same.

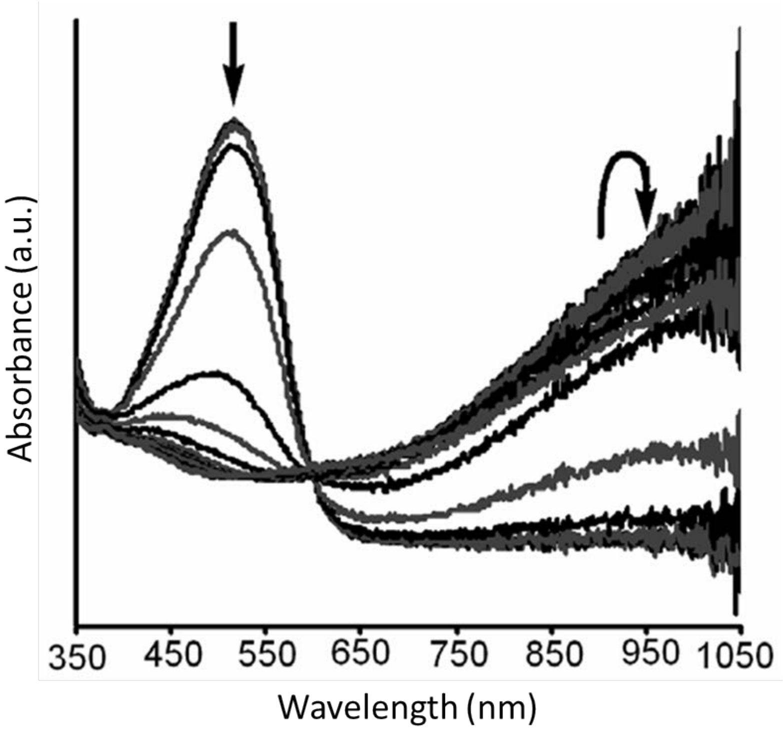

Figure 2. Spectroelectrochemical data for bisEDOT obtained in 0.1 M TBAPF6 in DCM (every other scan is grey).

Spectroelectrochemistry

Spectroelectrochemical data was obtained to further investigate the intriguing properties of poly(bisEDOT). The polymer was grown on an indium-doped tin oxide coated glass electrode (ITO) from a 2.5 mM solution of BISEDOT in 0.1 M $TBAPF_6$ in DCM. This allowed for recording UV-visible spectra of the polymer while varying the potential at which it is held. For the neutral polymer, the maximum wavelength of absorption was observed at 515 nm. The polaronic peak, which began growing in when the polymer was held at 0.19 V, was observed at approximately 985 nm. There is no real increase in the polaronic peak in going from 0.5 V to 0.62 V. The peak then begins to decrease when the polymer is held at and above 0.69 V. The broad absorption peaks that have been observed thus far for methano[10] annulene-containing polymers were also evident here. However, unlike the other methano[10]annulene polymers we have studied, there appeared to be a clear isosbestic point present in this spectrum suggesting some amount of charge localization within the polymer (Figure 2). The polymer showed some electrochromic properties in that when the polymer was fully reduced it was a reddish pink color and when it was fully oxidized it was of a light grey color.

Atomic Force Microscopy

Atomic force microscopy was used to determine the morphology of the bisEDOT-SMA thin film after *in situ* oxidative polymerization with bromine (Figure 3). Previous investigations of bisEDOT-SMA thin films have shown that after deposition the films are smooth and no fine structure was observed. However, after polymerization, we observe two sets of features. From power spectrum density (PSD) curve and FFT measurements we find that the smaller features are the cylinder domains which are approximately 1 nm tall elevations with a periodicity of 27 nm. The larger features reach heights of 5 nm and are randomly distributed throughout the surface. We believe that both of these features are poly(bisEDOT which protrudes slightly from the surface of the BCP film as a result of polymerization.

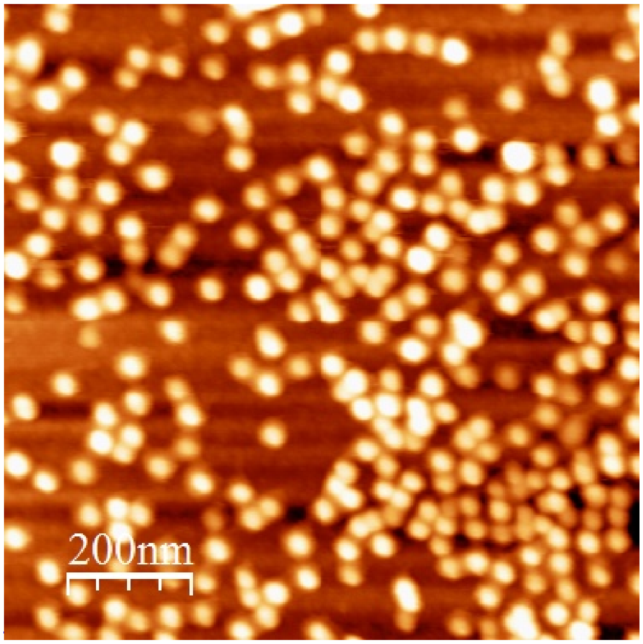

Figure 3. 1.0 x 1.0 µm AFM topography image of a bisEDOT-SMA thin film (left) after *in situ* polymerization with bromine and washed with toluene to remove the template.

Spectroscopic Ellipsometry was used to reveal the porosity of the SMA film upon extraction of bisEDOT (Figure 4). The best fit using EMA approach gives the porosity of 0.171 (linear model, Figure 5) and 0.125 (Garnett-Maxwell).

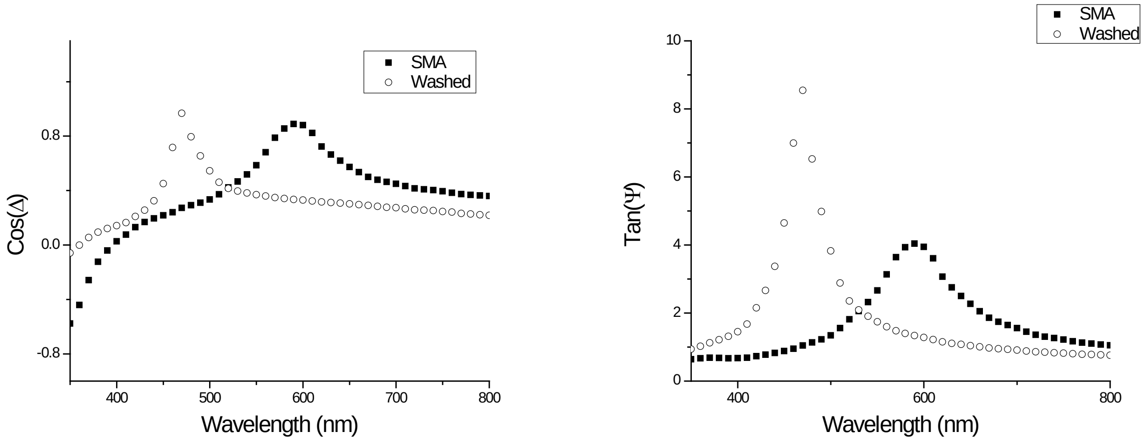

Figure 4. Ellipsometric spectra (profiles) of Δ and Ψ obtained for 100 nm thick film of SMA before (filled squares) and after (hollow circles) extraction of bisEDOT.

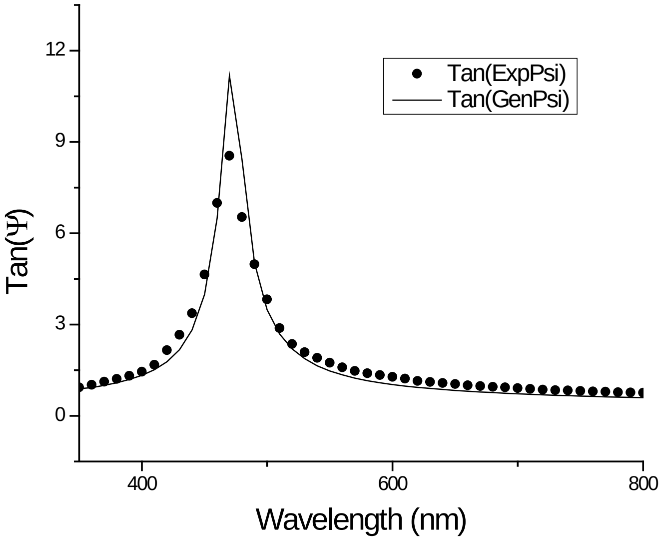

Figure 5. tanΨ profile of the SMA film (100nm thick) upon bisEDOT extraction (dots) and best fit (17.1% porosity) obtained using linear model EMA (red line).

Transmission Electron Spectroscopy was done with a Tecnai 12 G2 Spirit instrument (FEI Company, US). The samples were deposited on glass slides, washed in methanol, and stained by I_2 from its vapors. The films were transferred onto epoxide slab. Cross-sections of 80nm in thickness were prepared with an ultramicrotome.

The results of cross-section TEM are shown in Figure 6. The TEM images reveal poorly ordered cylinders, yet preferentially parallel to the surface. The diameter of the cylinders approximately 14 nm and the center-to-center distance (periodicity) of about 27 nm, in good agreement with AFM data.

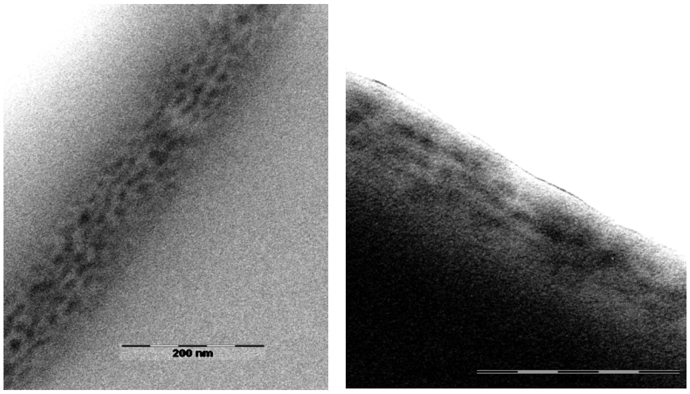

Figure 6. Cross-section TEM images of stained porous films either one-side (right) or two-side embedded into epoxide. Both bars are 200 nm. Number of elongated dark features (iodine stained P4VP) infers cylindrical morphology.

References

1. Q. Pei, G. Zuccarello, M. Ahlskog and O. Inganas, *Polymer*, 1994, **35**, 1347.
2. P. A. Peart and J. D. Tovar, *Org. Lett.* , 2007, **9**, 3041.
3. P. A. Peart and J. D. Tovar, *Macromolecules*, 2009, **42**, 4449.