Vibrational Spectroscopy and Molecular Simulation of Thiophene Polymerization

Shrirang Chhatre (Shrirang@udel.edu); Vivek Subramanian, D. Bruce Chase, David C. Martin
Department of Materials Science and Engineering, University of Delaware, Newark–19716

Introduction

- Conjugated polymers have been of recent interest in biomedical devices due to their ability to conduct both electronically and ionically, which makes them ideal for interfacing soft ionically conducting tissues with electron conducting metals.
- Poly(3,4-ethylenedioxythiophene) or PEDOT has received particular interest due to its chemical and mechanical stability. There has been considerable focus on the design, synthesis and characterization of functionalized PEDOT conjugates.
- A major limiting in this effort has been the insolubility of PEDOT in most known solvents; this makes molecular weight measurements by conventional techniques like Column Chromatography, Gel Permeation Chromatography essentially impossible.
- Here, we examine the use of vibrational spectroscopy techniques to obtain insights about the electrochemical polymerization of PEDOT.

Electrochemical Polymerization

- PEDOT was electrochemically polymerized in water on a 0.5 cm x 0.5 cm Indium Tin Oxide working electrode passing a constant current of 75 μA for 600 seconds. Water was used as a solvent with LiClO4 as a counter ion.
- A dark blue film of PEDOT develops on the electrode.

In-Situ TEM imaging of electrochemical deposition of PEDOT

- Low dose (0.1-1mC/cm2), in-situ transmission electron microscopy (TEM) was used to image the early stage nucleation processes and the liquid to solid transitions involved in the polymerization process.

Gaussian Simulations

- Geometry Optimization and Frequency calculations were performed on EDOT and its oligomers to identify critical peaks which could give us an indication about polymerization.
- DFT calculations were performed with the 631G(d,p++) basis set with a tight convergence criterion.
- Using the spectral data of EDOT, EDOT oligomers and EDOTacid we were able to assign peaks corresponding to the various vibrational modes as shown by the Gaussian calculations with confidence.

Experimental Results

- The patterns of EDOT and PEDOT were compared and peak assignments were made. Additionally EDOT and EDO Tacid Raman spectra was measured.
- A comparison of the Raman spectra for EDOT, PEDOT and EDO Tacid was done and the peaks were tabulated.
- A peak is seen at 1501 cm⁻¹ which is associated with the quinoid C=C stretch.
- An antisymmetric benzoïdal C–C stretch develops at 1601 cm⁻¹ and then shows a redshift for the trimer. Correlating strongly with DFT calculations, this trend continues for higher oligomers as shown with the calculations.
- Conversely we see a blueshift for the symmetric C=C stretching vibration which is also consistent with our experimental data. We expect this mode’s intensity to stay relatively constant; with minor changes due to coupling effects.
- Additionally, the peak seen at 1422 cm⁻¹ has been identified in the literature as the C=C stretching vibration which is also consistent with our experimental data. We expect this mode’s intensity to stay relatively constant; with minor changes due to coupling effects.
- The C–H stretching region (2800–3200 cm⁻¹) is of special interest to us, since the thiophene proton is the reactive proton in our reaction. We are carefully examining modes that could indicate the progress of the polymerization reaction.

Relative Intensity Model

- There is strong correlation between experimental and simulation data to suggest that the mode at 380 cm⁻¹ corresponds to the thiophene C–H stretch. We expect this mode’s intensity to stay relatively constant; with minor changes due to coupling effects.
- Additionally, the peak seen at 1424 cm⁻¹ has been identified in the literature as the C=C stretching vibration which is also consistent with our experimental data. We expect this mode’s intensity to stay relatively constant; with minor changes due to coupling effects.
- We plotted the theoretically predicted ratio of the relative intensity of these peaks as a function of oligomer length to give us a model for analyzing our PEDOT data.

Conclusions and Future Work

- We have developed a model for molecular weight estimation of PEDOT oligomers using experimental and simulated Raman spectra.
- We demonstrated its potential utility in differentiating oligomer lengths and reaction optimization.
- Correlations of Raman spectroscopy data with in-situ TEM experiments should give us valuable insights into the physical transformations correlated with chemical changes.
- A higher degree of correlation between experimental and simulated results can be obtained through geometrical optimization forcefield calculations combined with experimental data.
- Thus, we can track polymerization in insoluble hard to characterize polymers.

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