Organic Electronic Devices

Week 1: Semiconductor Synthesis and Characterization
Lecture 1.5: Structural and Optical Characterization

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Lecture Overview and Learning Objectives

• Concepts to be Covered in this Lecture Segment
  • Crystallinity and Crystal Structures in Organic Semiconductors
  • Bulk vs. Thin Film Structural Measurements
  • Solution and Solid State Optical Characterization Methods

• Learning Objectives
  By the Conclusion of this Presentation, You Should be Able to:

1. **Utilize** Bragg’s Law and the definition of the wave vector to calculate domains spacings in organic semiconductors.

2. **Explain** how grazing-incidence wide-angle x-ray scatting (GI-WAXS) can be used to quantify the alignment of crystallites in polymer thin films and **describe** how atomic force microscopy (AFM) can image these crystalline domains directly.

3. **Employ** Beer’s Law to estimate the concentration of an organic semiconductor in solution and to calculate the absorption coefficient of organic semiconductors given the thickness of the thin film.
Crystallinity in Polymers Goes Across Multiple Length Scales

- When the polymer chains are in solution or heated above the melting transition and in a liquid-like state (typically called the melt), they are isolated from one another and do not crystallize.

- The individual polymer chains begin to organize into small regions of high order generally referred to as crystallites.

- If given the proper amount of time or through the use of external stimuli, these small grains can organize into longer ranges of order.
**Classic Semiconducting Polymer Crystal Structure: P3HT**

P3AT Crystal Schematic

alkyl stacking direction, (h00)

chain axis direction, (00l)

$\pi-\pi$ stacking direction, (0k0)

Evaluating Crystal Structures Using X-Ray Scattering

Bragg’s Law of Diffraction

\[ \lambda = 2d \sin \theta \quad ; \quad q = \frac{2\pi}{d} \]

- \(\lambda\): Wavelength of Incoming Light
- \(d\): Spacing Between Crystal Planes
- \(\theta\): Angle Made Between the Crystal Plane and the Incoming Light
- \(q\): Scattering Vector

P3AT Examples

Linear Intensity (a.u.)

\[ q \text{ (nm}^{-1}\text{)} \]

0 5 10 15 20 25

- P3EHT
  - (010)
  - (100)
  - (200)

- P3DDT
  - (010)
  - (100)
  - (200)
  - (300)

- P3HT
  - (010)
  - (100)
  - (200)
  - (300)
Polymers Will Always Contain Some Amorphous Domains

Crystallization in Polymer Semiconductors Balances Thermodynamic Forces and the Desire of the Polymer Chains to Remain Flexible

The crystallite size scales between the ~10 nm scale and the ~1 mm scale. Therefore, it is likely that a charge will have to traverse one or more amorphous regimes in order to exit a macroscopic device.

Maximizing the degree of crystallinity and the alignment of the crystalline domains in the solid state is important in order to maximize charge transport in macroscopic devices.
Evaluating Crystal Structure and Orientation in Thin Films

Grazing-Incidence Wide Angle X-Ray Scattering (GI-WAXS)

Monochromatic X-Ray Beam

X-Ray Source

Substrate (SiO₂)

Beamstop

“Transmitted” Beam

P3AT Thin Film
We Are Able to Watch P3ATs Crystallize in Real-Time

(100) Bragg Reflection

Grazing Incidence XRD

Relative Crystal Orientation

Thin Film Crystallites Can Be Imaged Directly

Films were spun from a 10 mg/1 mL chloroform solution at 1000 rpm for 60 sec. Final film thicknesses were ~80 nm.

Quantification of the Optical Properties of Semiconductors

Ultraviolet-Visible (UV-Vis) Light Spectroscopy

Allows for the quantification of the absorption of small molecule and polymer semiconductors in the ultraviolet and visible (and even the infrared) portions of the electromagnetic spectrum.

Beer’s Law in Solution

\[ A = \varepsilon b C \]

Beer’s Law in the Solid State

\[ I = I_0 e^{-\alpha d} \]

Large Difference in Absorption Between Solution and the Solid States

Polymers in ~1 μM chloroform solutions


The Shift to Lower Wavelengths (Red Shift) is Due to Solid State Aggregation
The bulk and thin film crystal structure and crystal texture of organic semiconducting materials is of critical concern in terms of the final optoelectronic properties of the materials. Traditionally, these properties can be characterized by x-ray scattering and microscopy in a rather straightforward manner. The larger the size of the crystalline grains usually points to better charge transport as it minimizes the number of amorphous domains that must be crossed by the charges in the solid state.

UV-Visible light absorption spectroscopy allows researchers to characterize the optical transitions (and magnitude of absorption) for organic semiconductors both in solution and in the thin film state. Many times, the optical absorption of organic semiconductors will be red-shifted relative to their absorption spectra in solution. The thin film absorption coefficient of many organic semiconductors is between $10^4$ and $10^5$ cm$^{-1}$. 

Next Time: Atomic and Molecular Orbital Theory