Organic Electronic Devices

Week 1: Semiconductor Synthesis and Characterization

Lecture 1.1: An Introduction to Organic Electronic Materials

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Lecture Overview and Learning Objectives

- **Concepts to be Covered in this Lecture Segment**
  - Chemical Structures of Organic Semiconductors
  - Nomenclature of Common Organic Semiconducting Materials
  - Design Considerations for Small Molecule and Macromolecular Organic Semiconducting Materials
  - Molecular Weight Characterization of Polymer Semiconductors

- **Learning Objectives**

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

  1. **Draw** the chemical structure of a common organic semiconductor given the name and/or **recite** the name of an organic semiconductor given the chemical structure of the material.
  2. **Predict** the relative properties of two organic semiconductors given the chemical structure of the two materials.
  3. **Calculate** the number-average molecular weight, weight-average molecular weight, and dispersity of a semiconducting polymer.

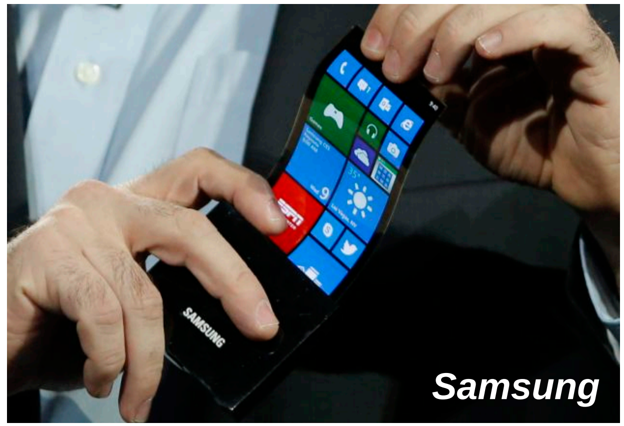
Understanding Device Operation Requires Knowledge of Materials

Organic Light-emitting Device (OLED) Displays

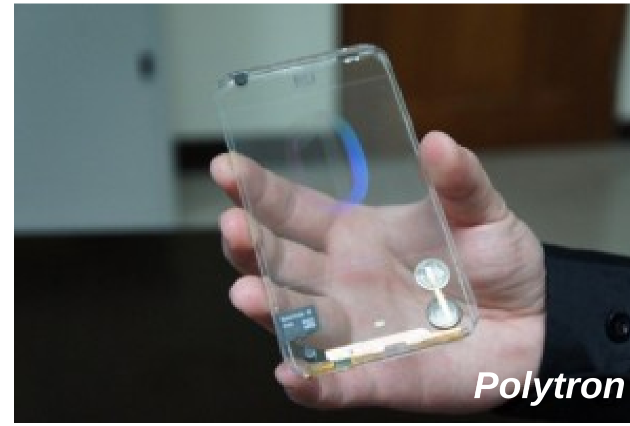
Thin and Lightweight


Sony

Flexible

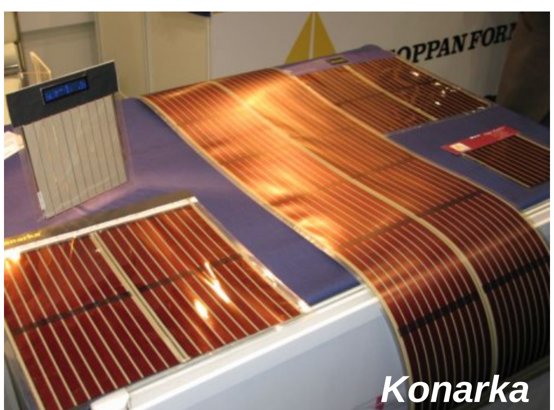

Samsung

Transparent


Polytron

Organic Photovoltaic (OPV) Devices

Large Area Production


Konarka

Portable Applications


Konarka

Conformal Coverage


Konarka

General Characteristics of Organic Semiconductors

- In this course, an organic semiconductor has the following properties.

1. The material is **composed primarily of carbon, hydrogen, and oxygen.** Other atoms may be present in the material, but the majority (> 90%) of the mass in these materials will be hydrocarbon-based.

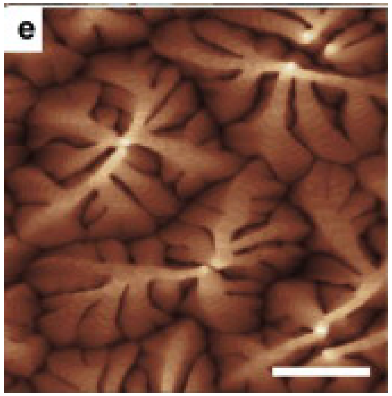
2. In general, the organic semiconductors will contain a great deal of alternating single and double bonds (***i.e.*, they are π-conjugated materials**).

3. Organic semiconductors are **van der Waals solids that have covalent bonds** between the atoms of the materials.

Single Crystals

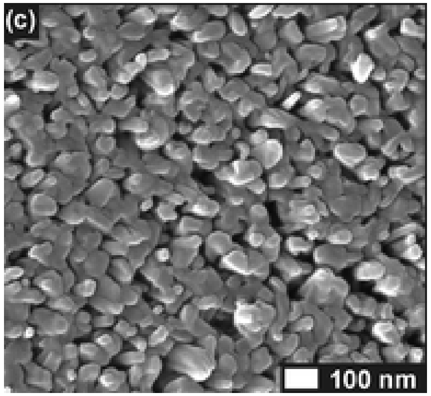
Podzorov Research Group, http://www.physics.rutgers.edu/~podzorov/index.php

Semicrystalline



Tonazzini, I.; *et al. Biophys. J.* **2010**, *98*, 2804.
Scale Bar = 1 μm

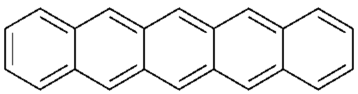
Nearly Amorphous



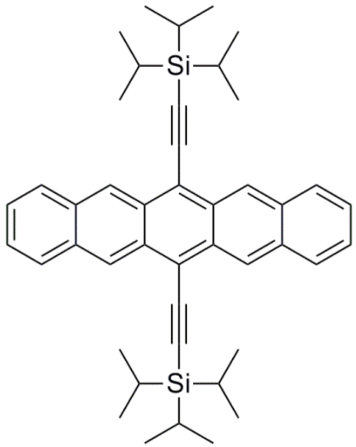
van Dijken, J. G.; Fleischauer, M. D.; Brett, M. J. *J. Mater. Chem.* **2011**, *21*, 1013.

Commonly-used Small Molecule Organic Semiconductors

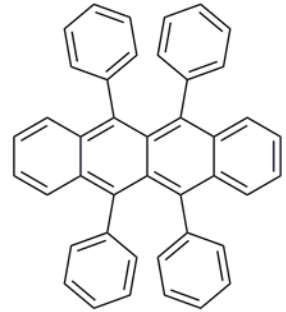
Primarily Hole Transporting (p-type) Organic Semiconductors



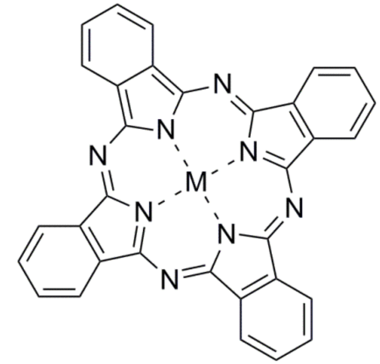
Pentacene



TIPS-Pentacene



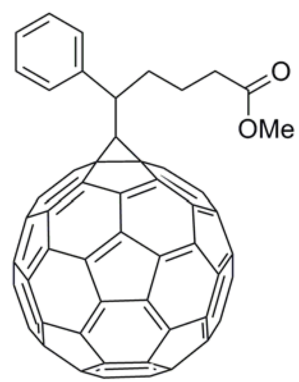
Rubrene



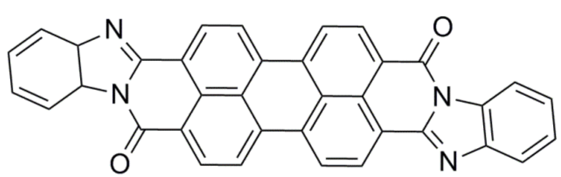
Metal (e.g., Cu or Zn) Phthalocyanines (Pc)

Primarily Electron Transporting (n-type) Organic Semiconductors

Buckminsterfullerene (C_{60})



PCBM

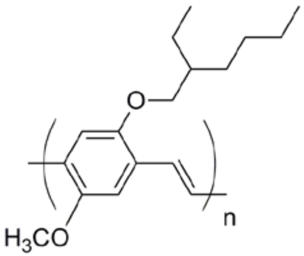


PTCBI

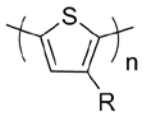
Further Reading: Mishra, A.; Bäuerle, P. *Angew. Chem. Int. Ed.* **2012**, *51*, 2020.

Commonly-used Polymeric Organic Semiconductors

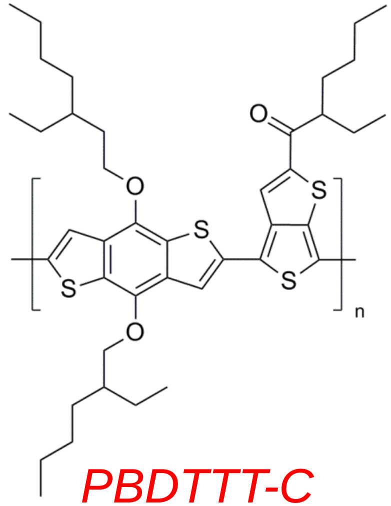
Primarily Hole Transporting (p-type) Polymer Semiconductors



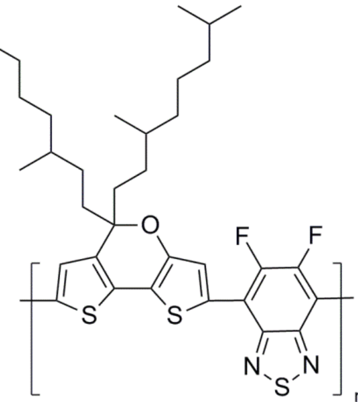
MEH-PPV



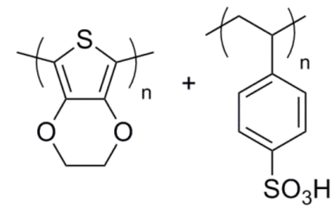
P3AT



PBDTTT-C

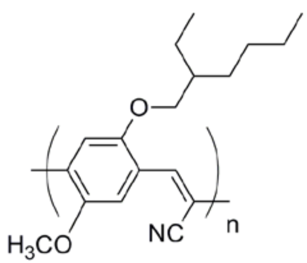


PDTP-DFBT

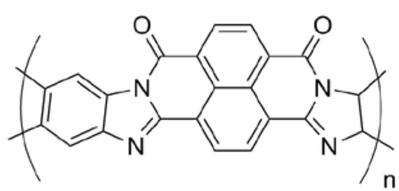


PEDOT:PSS

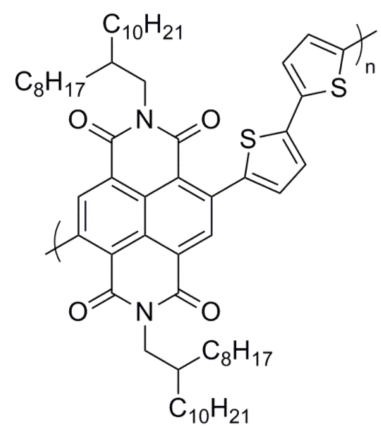
Primarily Electron Transporting (n-type) Polymer Semiconductors



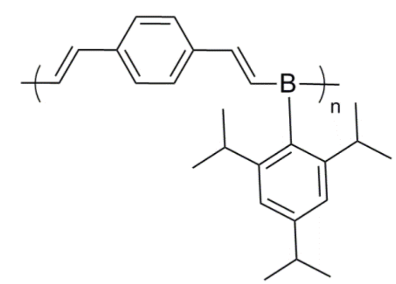
CN-MEH-PPV



BBL



P(NDI2OD-T2)



PT01

Further Reading: Boudouris, B. W. *Curr. Opin. Chem. Eng*. **2013**, *2*, 294.

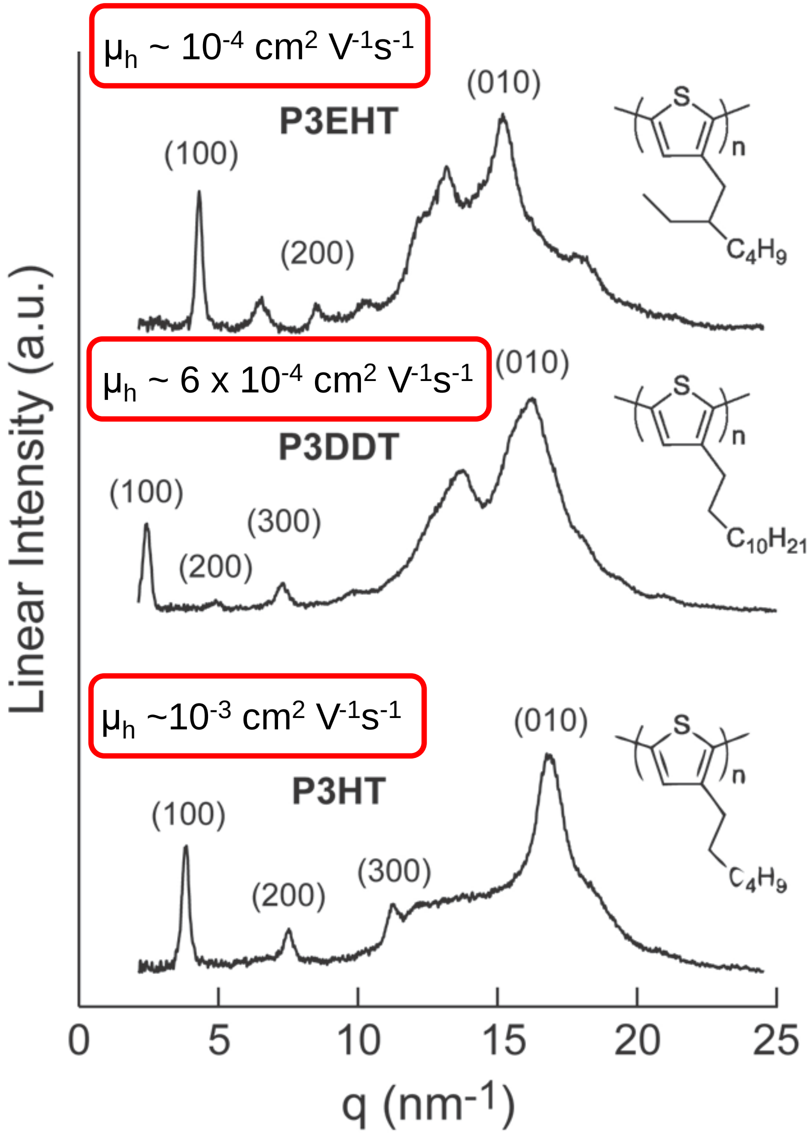
Design Considerations for Polymer Electronic Materials

- Increases in Polymer Backbone Conjugation and Thin Film Crystallinity Tends to Improve the Charge Transport Ability
  - Higher Molecular Weight Leads to Higher Degrees of Crystallinity
  - Narrow Molecular Weight Distributions Lead to Higher Degrees of Crystallinity
  - Fused Rings Add to the Degree of Conjugation of the Polymer. This Leads to More Charge Delocalization and, Generally, To a Better Ability to Transport Charge

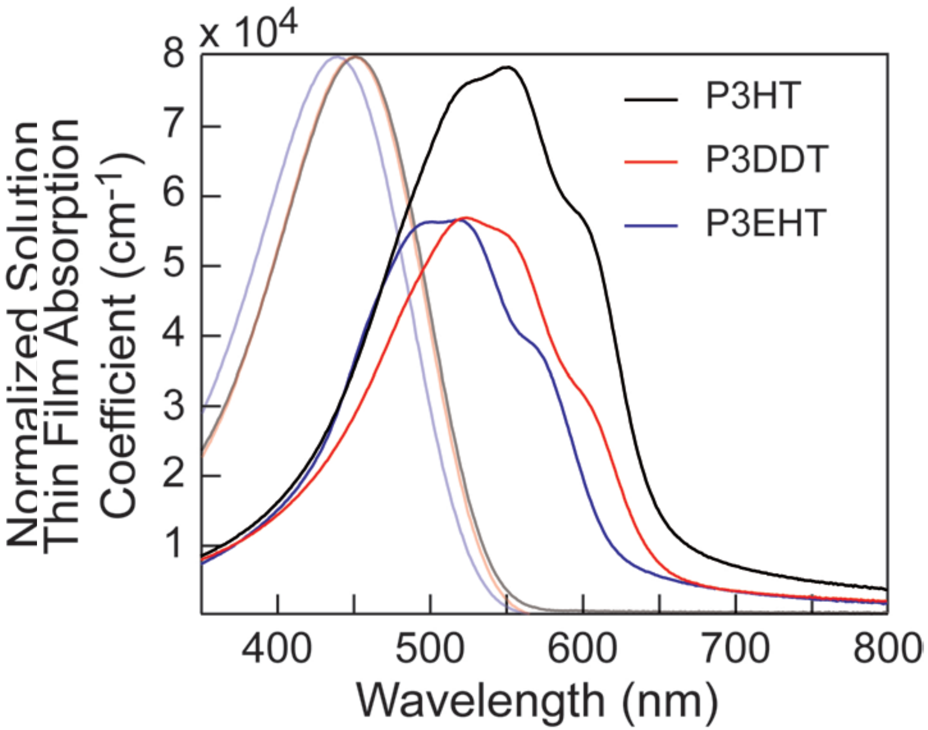
- Side Chains Are Used to Increase Solubility But Can Have Secondary Effects with Respect to Thin Film Structure
  - Branched Side Chains Help Increase the Solubility of the Organic Electronic Materials Greatly
  - Side Chains Can Impact the Thermal, Structural, and Optoelectronic Properties of the Polymers by Changing the Solid State Packing

Case Study: Poly(3-alkylthiophenes) (P3ATs)

Powder WAXS Patterns



UV-Vis Absorption Spectra



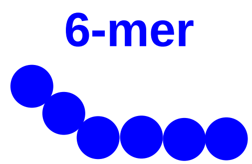
Polymers in ~1 μM chloroform solutions

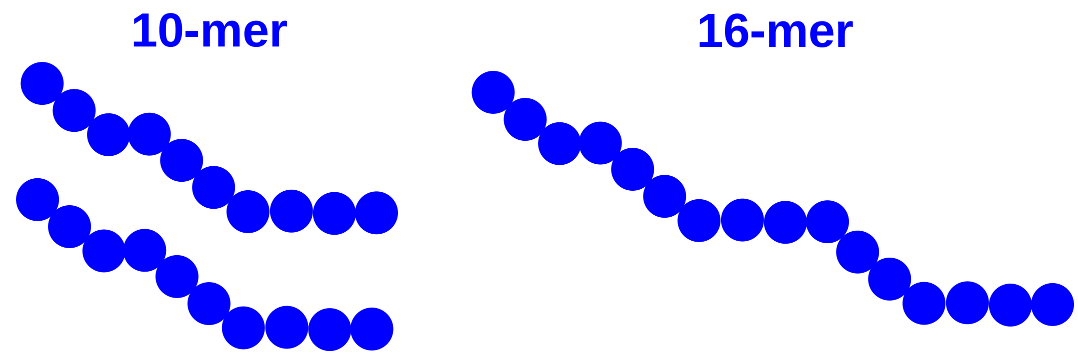
Spun-coat from chloroform for a
Final film thickness of ~80 nm

Further Reading: Ho, V.; Boudouris, B. W.; Segalman, R. A. *Macromolecules* **2010**, *43*, 7895.

Determination of the Number-average Molecular Weight (M_n)

Polymers Contain a Mixture of Macromolecular Sizes





M_0 = 100 g mol^{-1}

Molar Mass of a Repeat Unit: M_0

Molecular Weight of an *i*-mer with *i* number of repeat units: $M_i = i \times M_0$

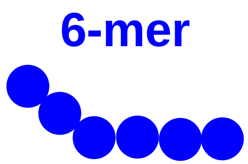
Mole Fraction of an *i*-mer: $x_i = \dfrac{n_i}{\sum_i n_i}$

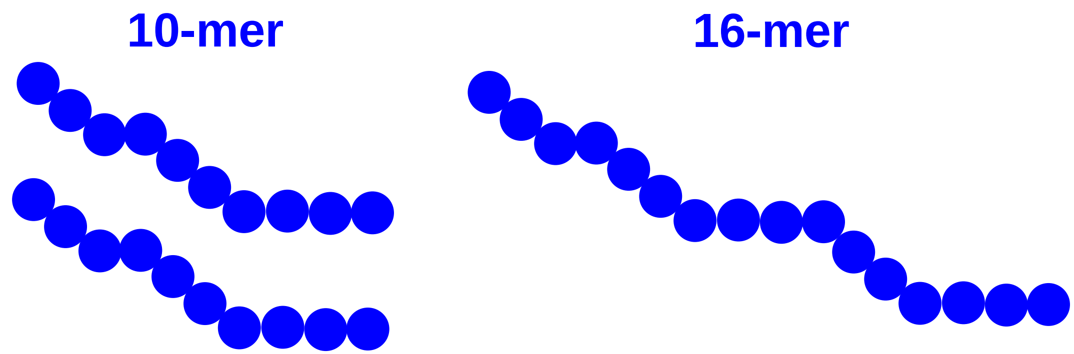
Number-average Molecular Weight: $M_n = \sum_i x_i M_i = \dfrac{\sum_i M_i n_i}{\sum_i n_i} = M_0 \dfrac{\sum_i i n_i}{\sum_i n_i}$

$$M_n = M_0 \frac{\sum_i i n_i}{\sum_i n_i} = \left(100\ g\ mol^{-1}\right) \times \frac{(1\times 6) + (2\times 10) + (1\times 16)}{1+2+1} = 1{,}050\ g\ mol^{-1}$$

Determination of the Weight-average Molecular Weight (M_w)

Polymers Contain a Mixture of Macromolecular Sizes





M_0 = 100 g mol^{-1}

Molar Mass of a Repeat Unit: M_0

Molecular Weight of an *i*-mer with *i* number of repeat units: $M_i = i \times M_0$

Weight Fraction of an *i*-mer: $w_i = \dfrac{in_i}{\sum_i in_i}$

Weight-average Molecular Weight: $$M_w = \sum_i w_i M_i = \frac{\sum_i in_i M_i}{\sum_i in_i} = M_0 \frac{\sum_i i^2 n_i}{\sum_i in_i}$$

$$M_w = M_0 \frac{\sum_i in_i}{\sum_i n_i} = \left(100\ g\ mol^{-1}\right) \times \frac{(1\times 6^2)+(2\times 10^2)+(1\times 16^2)}{(1\times 6)+(2\times 10)+(1\times 16)} = 1{,}171\ g\ mol^{-1}$$

Dispersity (Đ) and the Impact on Organic Electronic Devices

Dispersity is a Measure of the Molecular Weight Distribution

Dispersity of a Polymer: $Đ \equiv \frac{M_w}{M_n}$

Because: $M_w \geq M_n$, Then: $Đ \geq 1$

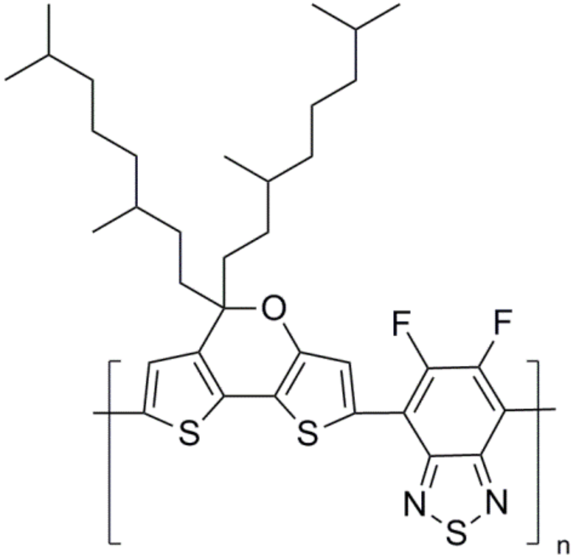
Dispersity Can Be Thought of in Terms of the Standard Deviation from the Average:

$$\sigma = M_n \left[\frac{M_w}{M_n} - 1 \right]^{1/2} = M_n \left[Đ - 1 \right]^{1/2}$$

Narrowing the Dispersity (*i.e.*, Minimizing the Standard Deviation in) of the Polymer Chains, Increases the Ability of the Polymer to Achieve a Higher Degree of Crystallinity. This, in turn, Increases the Charge Transport Ability of the Polymer in the Solid State.

Summary and Preview of the Next Lecture

Organic electronic materials are molecular solids that contain covalent bonds and are composed mainly of carbon, hydrogen, and oxygen. They contain a high degree of π-conjugation along the main chain of the molecules They can form crystalline domains on the order of millimeters, micrometers, or nanometers. The structure of the molecule dictates its optoelectronic properties.



Organic semiconductors The materials can either be small molecules or polymeric, and they can preferentially transport holes (p-type) or electrons (n-type). The selection of the functional groups along the polymer backbone and the degree of conjugation affect the optoelectronic properties of the material. Furthermore, side chains generally are used to increase the solubility of the semiconductor in solution; however, they can impact the optoelectronic properties as well. The number-average molecular weight, weight-average molecular weight, and the dispersity of a polymer can impact the crystallinity and optoelectronic properties of the materials.

Next Time: The Synthesis of Oft-Used Polymer Semiconductors