Organic Electronic Devices

Week 1: Semiconductor Synthesis and Characterization
Lecture 1.3: Synthesis of Low Bandgap Polymers

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Lecture Overview and Learning Objectives

• Concepts to be Covered in this Lecture Segment
  • Need for Low Bandgap Polymers
  • Concept of a Donor-Acceptor Polymer
  • Synthesis of Low Bandgap Polymers using the Siegrist, Stille, and Suzuki Coupling Reactions

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

1. **Define** what is meant by a low bandgap polymer and why these molecules are attractive for organic electronic applications.
2. **Draw** the reaction conditions for Siegrist, Stille, and Suzuki coupling reactions and required functionality of the monomers of these reactions.
3. **Predict** the products that would form from each of these types of reactions given the monomer units to be polymerized and/or **suggest** monomeric units and reaction method to use given a desired product.
Siegrist Polycondensation is Used for the Synthesis of PPVs

Reaction Notes

- This is a very simple reaction that can be performed in a straightforward manner (PRO).
- The chemistry leads to polymers with relatively low molecular weights \((M_n < 10 \text{ kg mol}^{-1})\) and broad molecular weight distributions \((\mathcal{D} > 2.0)\) (CON).
- Because of these two facts, extensive purification of the produced polymer is required for a number of applications (CON).
- Even after purification, the crystallinity values of PPV derivatives generally are relatively low (CON).

MEH-PPV is a Common PPV Derivative:
Definition of and Need for Low Bandgap Polymers

Absorbance of P3HT

\[ E = \frac{hc}{\lambda} \]

- \( E \) – Energy
- \( h \) – Planck’s Constant
- \( c \) – Speed of Light
- \( \lambda \) – Wavelength

\[ E_g (\text{P3HT}) = 1.9 \text{ eV} \]

Low Bandgap Polymers Are Highest Performing in OPVs

Electron Donor-Electron Acceptor Copolymers

- Species that are **Electron Rich** are capable of donating some of the local electron density.

- Species that are **Electron Poor (or Deficient)** are capable of accepting some of the local electron density.

- Combination of these two effects allows for a lowered energy and a lower bandgap energy.

**Further Reading:** Zhang, Z-G.; Wang, J. J. Mater. Chem. 2012, 22, 4178.
**Stille Coupling (Stille Polycondensation)**

**Stille Reaction Couples Di-stannanes and Di-aryl Halides to Form C-C Bonds**

\[(R)_3\text{Sn} - A - \text{Sn}(R)_3 + X - D - X \xrightarrow{\text{Catalyst}} [A - D]\]

**R:** Substituent that is usually chosen in order to make the tin-based material soluble in the reaction solvent

**X:** A common halide (usually Cl, Br, or I)

**Catalyst:** Usually palladium-based (Pd-based)

**Example of a Common Stille Coupling Polymerization**

**Red:** Stannanes

**Blue:** Aryl Halide

**Magenta:** New Carbon-Carbon Bond
Stille Coupling (Stille Polycondensation)

Stille Reaction Couples Di-stannanes and Di-aryl Halides to Form C-C Bonds

\[(R)_3Sn-A-Sn(R)_3 + X-D-X \xrightarrow{\text{Catalyst}} [A-D]\]

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**Reaction Notes**

- This is a very robust reaction in terms of the values of the A and the D groups. As such, many different conjugated polymers can be synthesized using this reaction (PRO).
- Generally, although not always, only low molecular weight species are formed. Also, it is difficult to generate polymers with low dispersity values (CON).
- It is difficult to remove the Pd catalyst in a complete manner (CON).
- This method is used to polymerize some of the highest performing organic electronic materials in use today (PRO).
Suzuki Coupling

Stille Reaction Couples Di-aryl or Di-Vinyl Boronic Acids and Di-aryl or Di-vinyl Halides to Form C-C Bonds

\[ \text{Y-B-A-B-Y} + \text{X-E-X} \xrightarrow{\text{Catalyst}} \text{A-E} \]

**Y:** Organoboric Acid-like Group

**X:** A common halide (usually Cl, Br, or I)

**Catalyst:** Usually palladium-based (Pd-based)

**Example of a Common Suzuki Coupling Polymerization**

**Red:** Boronic Acids

**Blue:** Aryl Halide

**Magenta:** New Carbon-Carbon Bond
Suzuki Coupling

**Stille Reaction Couples Di-ary1 or Di-Vinyl Boronic Acids and Di-aryl or Di-vinyl Halides to Form C-C Bonds**

\[
\begin{array}{c}
\text{Y–B–A–B–Y} \\
\downarrow \quad \downarrow
\end{array}
\quad +
\quad \begin{array}{c}
\text{X–E–X}
\end{array}
\quad \xrightarrow{\text{Catalyst}}
\quad \begin{array}{c}
\{ A–E \}
\end{array}
\]

**Y**: Organoboric Acid-like Group

**X**: A common halide (usually Cl, Br, or I)

**Catalyst**: Usually palladium-based (Pd-based)

**Reaction Notes**

- This is a very robust reaction in terms of the values of the A and the E groups (PRO).
- The limiting factor is the ability to synthesize the aryl boronic acid groups (CON).
- This reaction generally is less sensitive to oxygen than Stille Coupling (PRO), but gives about the same molecular weights and dispersity values as Stille Coupling (CON).
- It is difficult to remove the Pd catalyst in a complete manner (CON).
- This method is used to polymerize some of the highest performing organic electronic materials in use today (PRO).
The definition and need to synthesize low bandgap polymers was discussed. Furthermore, one strategy to fabricate low bandgap polymers \( (i.e., \) the internal electron donor-electron acceptor model) was detailed. From this point, the synthesis of these donor-acceptor materials using a variety of polymerization schemes was detailed.

The synthetic methodologies of the Siegrist Polymerization (to create PPV derivatives), the Stille polycondensation reaction, and the Suzuki coupling reaction were described. Also, specific examples of these reactions were detailed in order to provide guidance in the design of novel polymer semiconductors.

Next Time: Molecular and Thermal Characterization of Polymer Semiconducting Materials