Conducting Polymer

The chemistry Nobel prize in 2000 was awarded for the discovery and study of conducting polymers.

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Polymers

- Polymers are typically utilized in electrical and electronic applications as *insulators* where advantage is taken of their very high resistivities.

- Typical properties of polymeric materials: Strength, flexibility, elasticity, stability, mouldability, ease of handling, etc.
Conducting Polymers

• Can provide electromagnetic shielding of electronic circuits
• Can be used as antistatic coating material to prevent electrical discharge exposure on photographic emulsions
• Can be used as hole injecting electrodes for OLEDs
• Usage in electroluminescent displays (mobile telephones)
• In use as emissive layer in full-color video matrix displays
• Some are promising for field-effect transistors (Usage in supermarket checkouts)
• Some absorb microwaves: stealth technique
The **field-effect transistor (FET)** is a transistor that relies on an electric field to control the shape and hence the conductivity of a 'channel' in a semiconductor material. FETs are sometimes used as voltage-controlled resistors.

Large power N-channel field effect transistor
Conductivities

- Copper metal
- Polyacetylene doped with AsF$_3$
- Polyacetylene doped with I$_2$
- Liquid mercury
- Poly (p-phenylene) doped with AsF$_3$
- Poly (pyrrole) doped with I$_2$
- Polyaniline (emeraldine)

Logarithmic conductivity ladder locating some metals and conducting polymers
Oxidation States of PANI- octomers

**LEUCOEMERALDINE**  
Fully reduced

**EMERALDINE**

**NIGRANILINE**

**PERNIGRANILINE**  
Fully oxidized

-Neither the fully oxidized nor fully reduced state are conducting!
Figure 1

Overview of some of the potential applications of conducting polymers in microelectronics.
OLEDs

Model of conductivity in a polymer

Anode
"Hole-generator"
injects a hole
removes electrons

Cathode
injects electrons
removes holes

Conjugated polymers
insulators
semi-conductors
metals

Anode
Cathode
OLEDs - when electrons and holes meet

Jablonski Diagram

- Excited vibrational states (excited rotational states not shown)
- A = photon absorption
- F = fluorescence (emission)
- P = phosphorescence
- S = singlet state
- T = triplet state
- IC = internal conversion
- ISC = intersystem crossing

Electronic ground state
Known Structures

Advantages:
- Conjugated polymer
- Organic Light Emitting Device (OLED)
- Suitable for non-linear optics

Disadvantages:
- Practically insoluble
- Fluorescence is self quenching because of $\pi$-stacking
- Air and moisture sensitive
Shirakawa polyacetylene

- The polyacetylene film forms at the gas-liquid interface when acetylene gas passes through a heptane solution of the Ziegler-Natta catalyst.
- Cis polymer forms at low temperature (-78 °C). Isomerization to the more stable trans form takes place on rising the temperature of the film.
- Conductivity of doped cis films is two or three times greater than the trans analogues.
Polyacetylene (CH)$_x$ Shirakawa 2000 Nobel

$\text{C}_2\text{H}_2 \xrightarrow{\text{AlR}_3/\text{Ti(OR)}_4} \xrightarrow{\text{Ziegler Natta}} (\text{CH})_x$

- silvery film
- cis vs trans form, Temp. dependent
- semiconductor, BG = 1.9 eV

High temperature form: 100°C
Low temperature form: -80°C
-Mixture of Cis/Trans is formed by RT synthesis
-Cis form converts to Trans when mixture heated to 150°C

-Cis form- $10^{-9} \Omega^{-1}cm^{-1}$

-Trans form- $10^{-5} \Omega^{-1}cm^{-1}$

Thermodynamically more stable form
Catalytic polymerization of acetylene
- in the absence of $O_2$

1) Bubble acetylene thru solvent with catalyst
   - Solid PAc is precipitated

2) Acetylene gas- in glass tube coated with thin layer of catalyst
   - Best results for soluble catalyst(s)!
Ziegler-Natta likely involves acetylene insertion into M-R bonds

Also, ROMP synthesis- metathesis polymerization

catalysts: MoCl₆, WCl₆, Ta=CR₂, Cr=CR₂, Ta≡CR

Common by-product: Benzene, a cyclic trimer of acetylene
• As synthesized **conductive polymers** exhibit very low conductivities. It is not until an electron is removed from the valence band (p-doping) or added to the conduction band (n-doping, which is far less common) does a **conducting polymer** become highly conductive.

• **Doping** (p or n) generates **charge carriers** which move in an electric field. Positive charges (holes) and negative charges (electrons) move to opposite electrodes. This movement of charge is what is actually responsible for electrical conductivity.
“Synthetic Metals”

\[(\text{CH})_x\xrightarrow{\text{oxidation/reduction}} (\text{CH})_x^{\rho\pm}\]

chemical/
electrochemical

- metallic
- \(\sigma > 1000 \Omega^{-1}\text{cm}^{-1}\)

**Dopant types**
- Electron Acceptors: \(\text{Br}_2, \text{I}_2, \text{H}_2\text{SO}_4, \text{AsF}_5\)
- Electron Donors: Alkali Metals

- Conductivity increases very rapidly as dopant is added
- SC to insulator transition @ 1-5 mol %
  - much greater % dopant required than classical SCs like silicon (ppm levels)

- Expose to gasesous/liquid dopant
  - \((\text{CH})_n^{\delta^+} \text{Br}^{\delta^-}\) partial electron transfer occurs
  - Similar to Graphite…**Intercalation** of dopant
Doping is performed at much higher levels (20–40%) in conducting polymers than in semiconductors (<1%).

Figure 1. Removal of two electrons (p-doping) from a PT chain produces a bipolaron.
Figure 7.5. A: The layered structure of graphite. B: The oxidative intercalation of bromine into graphite removes electrons from the highest energy filled band in the graphite sheets (the sheets are represented by the parallel lines), while simultaneously forcing them further apart because of the intercalation of bromide ions between the layers.
Structure of $I_2$-doped trans-$(CH)x$
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Doping materials</th>
<th>$\Omega^{-1} \text{cm}^{-1}$</th>
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<tbody>
<tr>
<td>Polyacetylene</td>
<td>(CH)$_n$</td>
<td>I$_2$, Br$_2$, Li, Na, AsF$_5$</td>
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<tr>
<td>Polypyrrole</td>
<td></td>
<td>BF$_4^-$, ClO$_4^-$</td>
<td>500-7500</td>
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<tr>
<td>Polythiophene</td>
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<td>BF$_4^-$, ClO$_4^-$</td>
<td>1000</td>
</tr>
<tr>
<td>Poly(3-alkylthiophene)</td>
<td></td>
<td>BF$_4^-$, ClO$_4^-$</td>
<td>1000-10000</td>
</tr>
<tr>
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<td>AsF$_5$</td>
<td>500</td>
</tr>
<tr>
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<td></td>
<td>AsF$_5$</td>
<td>10000</td>
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<tr>
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<td>Polyaniline</td>
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<td>HCl</td>
<td>200</td>
</tr>
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</table>
Conjugation of $\pi$ orbitals

- $\sigma$ bond metal chain

- Overlap of electronic wave functions along the chain

  $\rightarrow$ anisotropic conductivity
  $\rightarrow$ conjugated chain through $\pi$ bond
Figure 2. Conjugated $\pi$-orbitals of a coplanar and a twisted substituted PT.

The twist in the backbone reduces the conjugation length (see Figure 2, bottom), and the separation between energy levels is increased. This results in a shorter absorption wavelength.
Conducting Mechanism

• While the addition of a donor or an acceptor molecule to the polymer is called "doping", the reaction that takes place is actually a redox reaction.

• The first step is the formation of a cation (or anion) radical, which is called a soliton or a polaron.

\[
P_n \Leftrightarrow [P_n^+ A^-] \\
(\text{reduction} \quad \text{oxidation})
\]
• This step may then be followed by a second electron transfer with the formation of a dication (or dianion) known as a bipolaron.

\[ \text{[Pn}^+ \text{A}^- \text{]} \Leftrightarrow \text{[Pn}^2+ 2\text{A}^- \text{]} \]
(reduction oxidation)

• Alternatively after the first redox reaction, charge transfer complexes may form between charged and neutral segments of the polymer when possible.

\[ \text{[Pn}^\bullet^+ \text{A}^- \text{]} + \text{Pm} \rightarrow \text{[(Pn Pm)}^\bullet^+ \text{A}^- \text{]} \]
Polarons & Bipolarons in oxidized Polythiophene

neutral chain

polaron

bipolaron
Oxidation States of PANI- octomers

**Fully reduced**

**Fully oxidized**

-Neither the fully oxidized nor fully reduced state are conducting!
Polymer-Based PV Devices

- Incident photons produce excitons, or bound electron-hole pairs, in both small molecule and polymer layers
- Excitons dissociate at small molecule-polymer interface, creating free electrons and holes
- The free charges travel through the respective transporting materials, creating a net current in the device
Polymer Selection

M3EH-PPV

poly[2,5-dimethoxy-1,4-phenylene-1,2-ethylenylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-1,2-ethylenylene]

- Hole-conducting polymer
- Donor: energy and/or charge transfer
**Polyacetylene battery**

**Anode:** \( \text{Ag} \rightarrow \text{Ag}^+ + e^- \)

**Cathode:** \( \text{I}_2 + 2e^- \rightarrow 2\text{I}^- \)

*Fig. 15. Solid state battery schematic for Ag|I\(_2\)|polyacetylene system: (1) copper, (2) silver lacquer, (3) graphite, (4) silver, (5) RbAg\(_4\)I\(_5\), (6) (CH\(_x\)), (7) Resin. [From Benerima et al. (1983).]*

silver paint

Ag

RbAg\(_4\)I\(_5\)

(CH\(_x\))

graphite
Ag$_2$HgI$_4$

(a) low-temperature order structure
(b) high-temperature disordered structure

a Ag$^+$-conductor
Use triiodide to oxidize polyacetylene as a means to measure glucose concentration.
Figure 7. PEDOT-PSS (Baytron-P) extensively used as an antistatic coating (as packaging materials for electronic components).

Figure 8. Ionoselective PTs functionalized with crown ethers reported by Bäuerle (left) and Swager (right).
Yashima and Goto found that a PT with a chiral primary amine was sensitive to chiral amino alcohols, producing mirror-image-split ICD responses in the $\pi$–transition region. This was the first example of chiral recognition by PTs using a chiral detection method/