

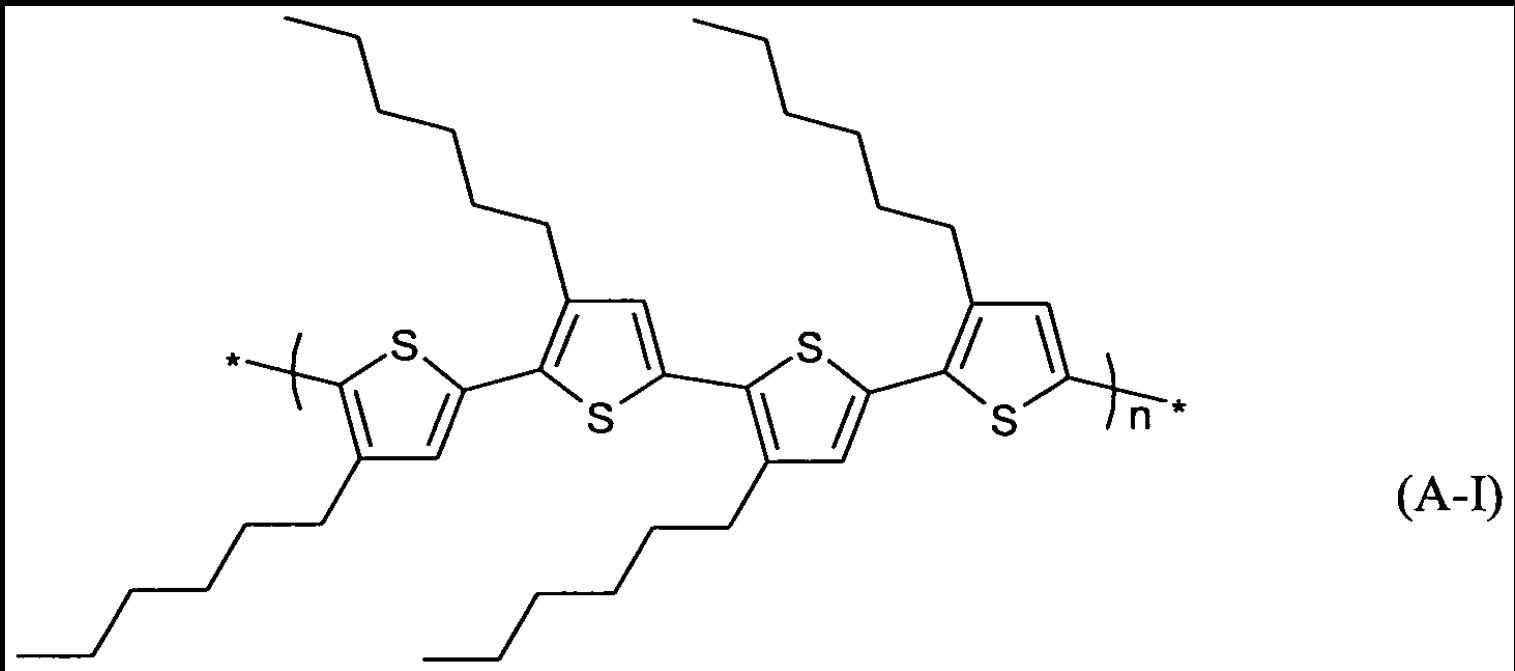
Conducting Polymers

Carly Anderson and Emily Davidson
April 23, 2013

Overview

- Background
- Motivation and History
- Insights into Solid State Physics
- Conduction, Doping, and Band Gap in Polymers
- New Horizons

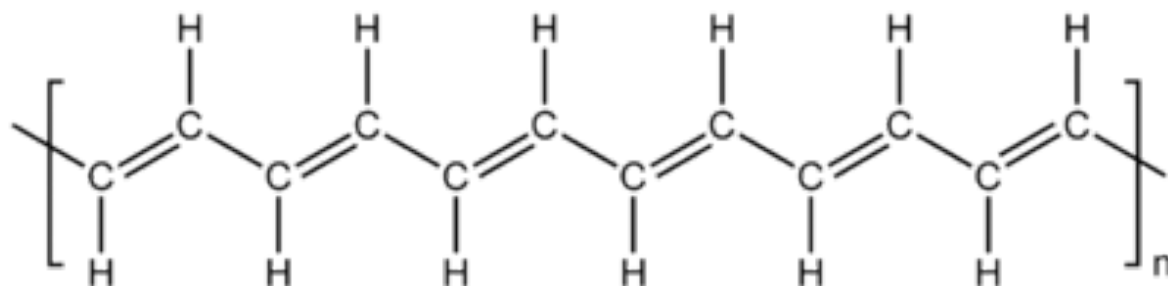
Background



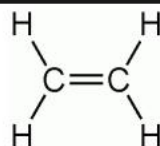
The structure of P3HT (Poly-3-Hexyl-Thiophene) a commonly studied conducting polymer

Basic Structure/Chemistry:

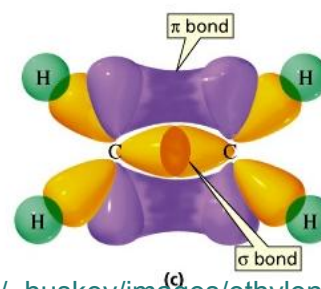
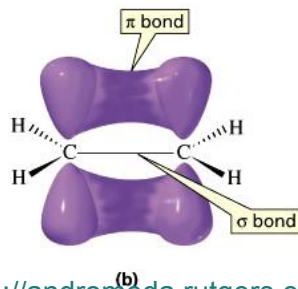
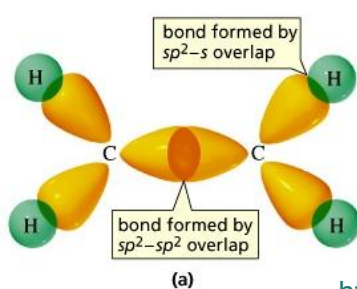
Polymers (Ex: Polyacetylene or Polyvinylene):



pi vs. sigma bonds:

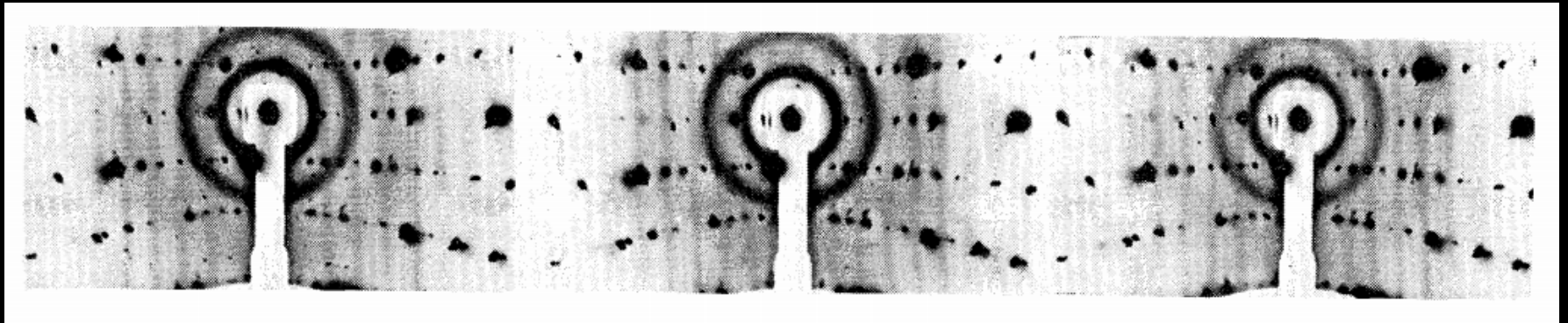


Ethylene (Ethene)



http://andromeda.rutgers.edu/~huskey/images/ethylene_bonding.jpg

Motivation and History



[Data confirming Peierls Transition]

F. Denoyer, F. Combs, A. F. Garito, and A. J. Heeger, *Phys. Rev. Lett.*, 1975, 35 (7).

http://prl.aps.org/abstract/PRL/v35/i7/p445_1

Why Conducting Polymers?

Uses for conductive polymers:

- The original thought: Replace copper in printed circuits and transmission lines with light, easy-to-process polymer materials
- Traditional applications: Corrosion inhibitors, compact capacitors, antistatic coating, “smart” windows
- New applications: transistors, organic light-emitting diodes (OLEDs), photovoltaics (OPVs), thermoelectric materials...

Advantages:

- Low cost
- Processibility

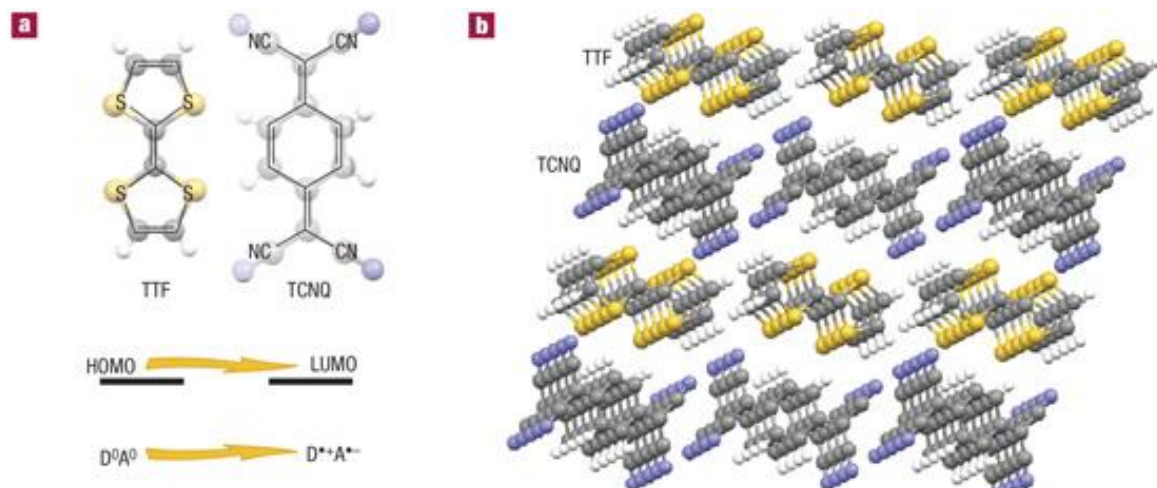
Disadvantages:

- Materials degrade
- High conductivity while maintaining processibility difficult

Early Development (1970's):

Interest in studying materials that are so anisotropic to effectively be 1-D systems

1st: X-ray Diffraction Study of TTF-TCNQ
(small molecule, quasi 1-D)

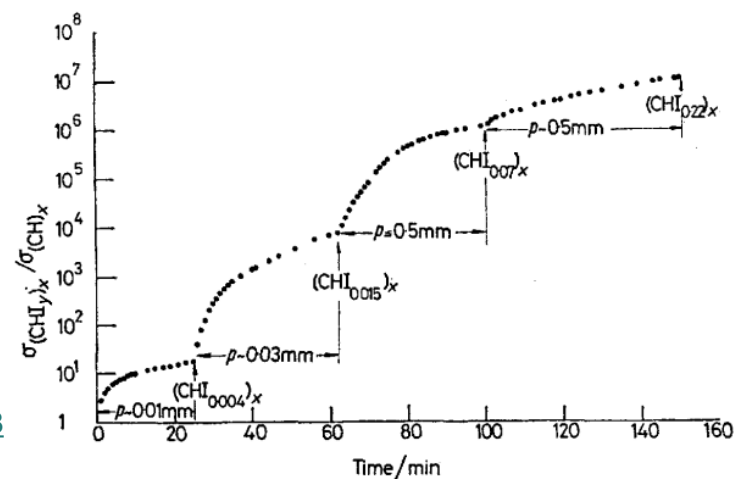


Early Development (1970's):

TTF-TCNQ, polyacetylene, and linear polymers displayed the 'Peierls Transition' (more on this later!)

Eftekhari, Ali. *Nanostructured Conductive Polymers*. 2010

Vapor-phase halogen doping of polyacetylene increased conductivity by 7 orders of magnitude!



This early work led to a Nobel Prize!



Alan J. Heeger



Alan G. MacDiarmid



Hideki Shirakawa

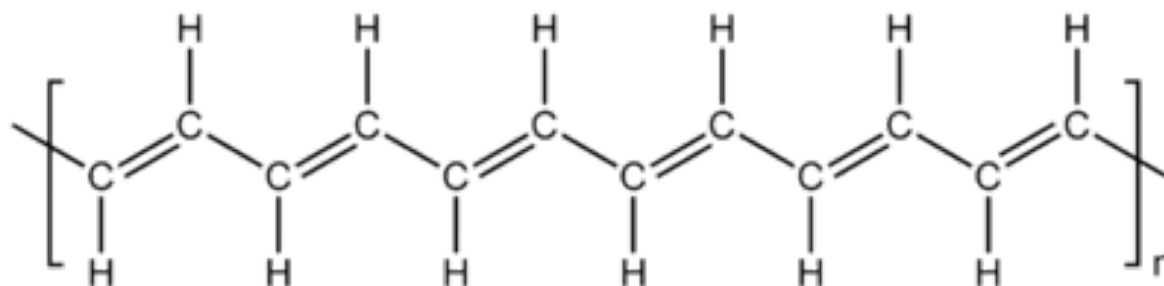
The Nobel Prize in Chemistry 2000 was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa *"for the discovery and development of conductive polymers"*.

Heeger, MacDiarmid, and Shirakawa won a Nobel for their original work done on polyacetylene in the 1970's.

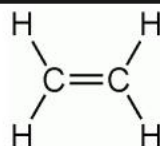
Conduction, Doping, and Band Gap in Polymers

Structure Reminder:

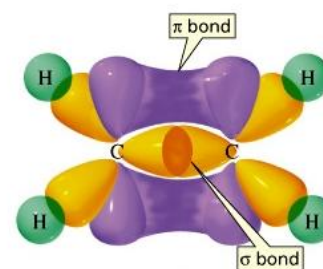
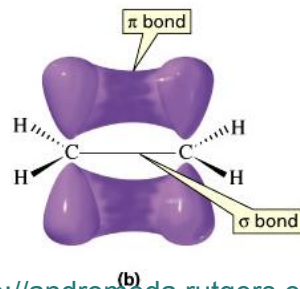
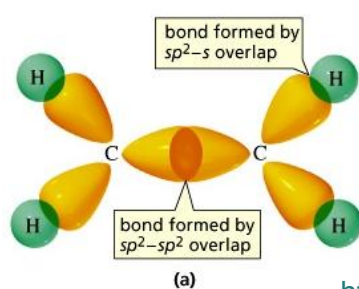
Polymers (Ex: Polyacetylene or Polyvinylene):



pi vs. sigma bonds:



Ethylene (Ethene)

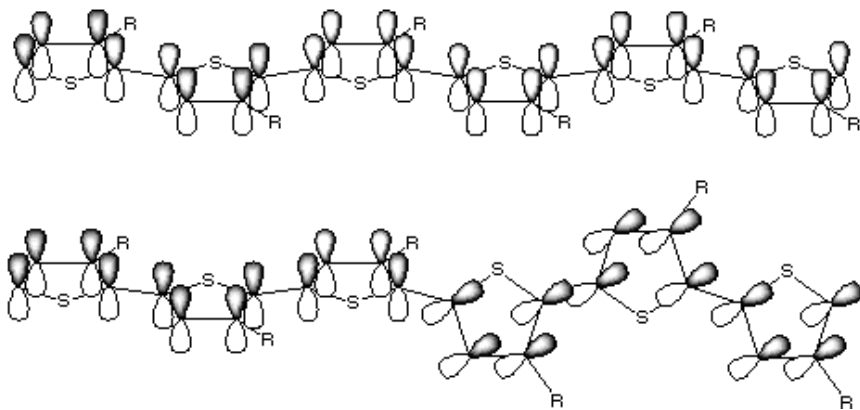


http://andromeda.rutgers.edu/~huskey/images/ethylene_bonding.jpg

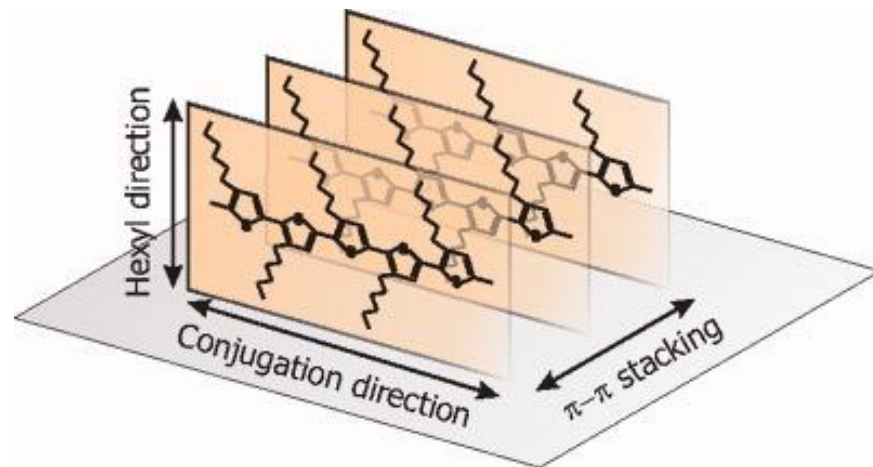
Charge Transport at the Molecular Scale:

Linear (conjugated pathways)

- Band pathways
- Variable-range hopping



Interchain/through stacks
(occurs in charge transport
polymers)

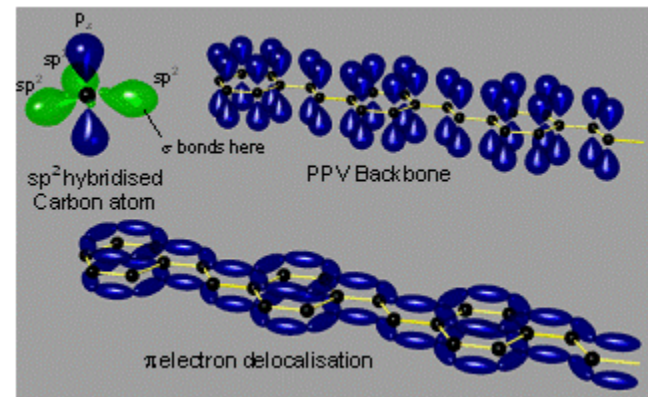


Conduction in Polymers: Bulk Behavior

Conductivity (σ) depends on density of charge carriers (n) and their mobility (μ). e is the charge of a single electron:

$$\sigma = n\mu e$$

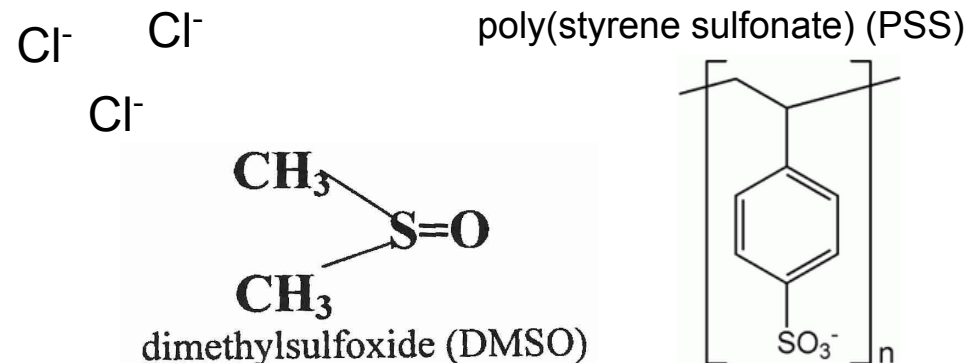
Density of charge carriers: In conjugated systems, one delocalized electron in the system of conjugated pi bonds per C atom.



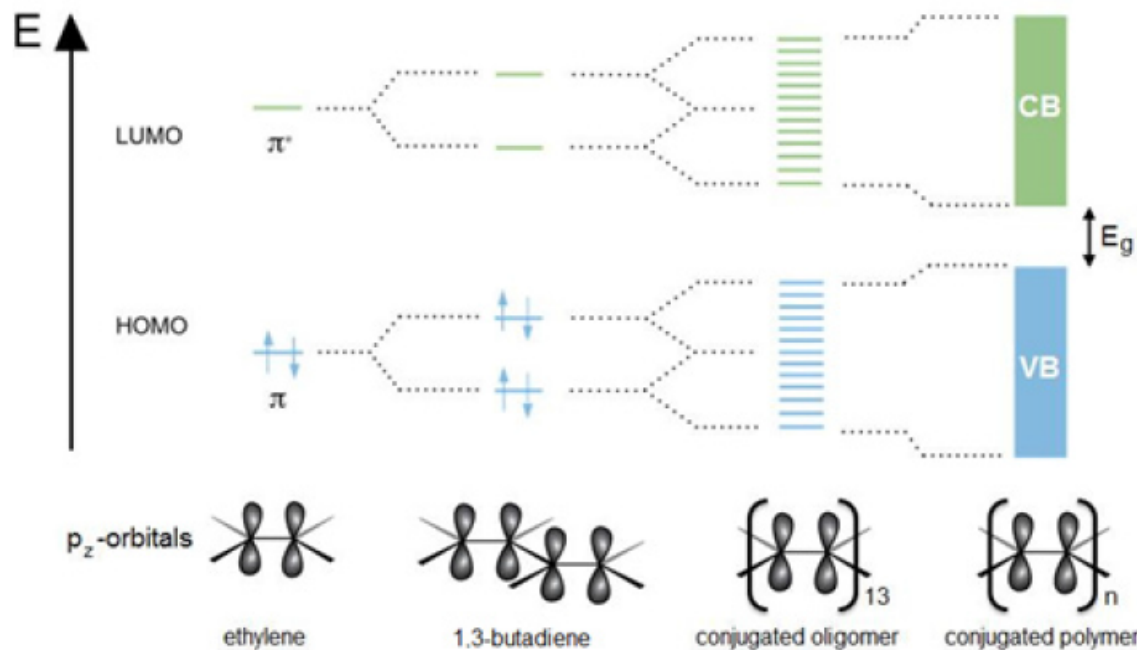
Polymer Doping:

- Polymers and semiconductors can both be doped by introducing additional charge carriers
- May be doped to much higher levels than semiconductors (up to 10-20% vs. ~1% for semiconductors)
- Many other mechanisms of doping including "structural dopants"

- Dopants may be ions (Cl^-), small molecules (DMSO), or other polymers (PSS)



Origin of Band Gap in Conjugated Polymers



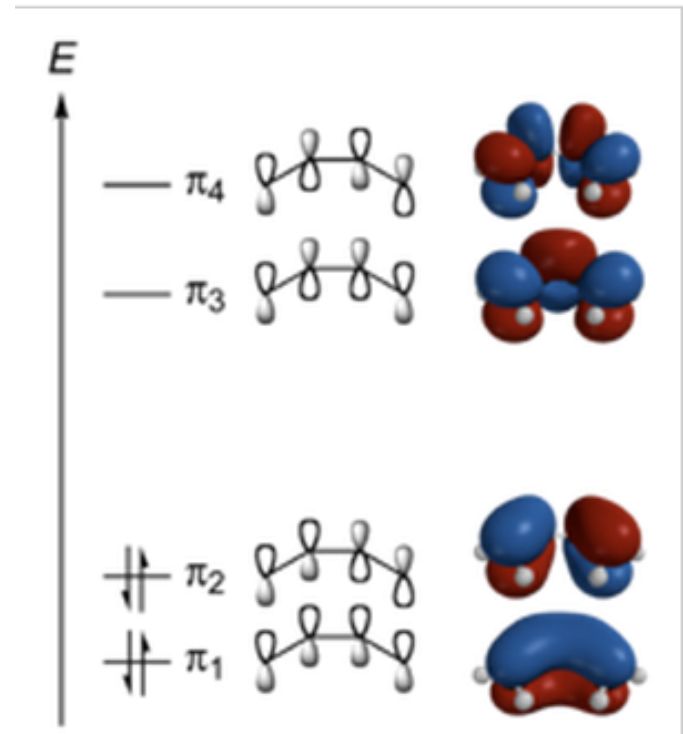
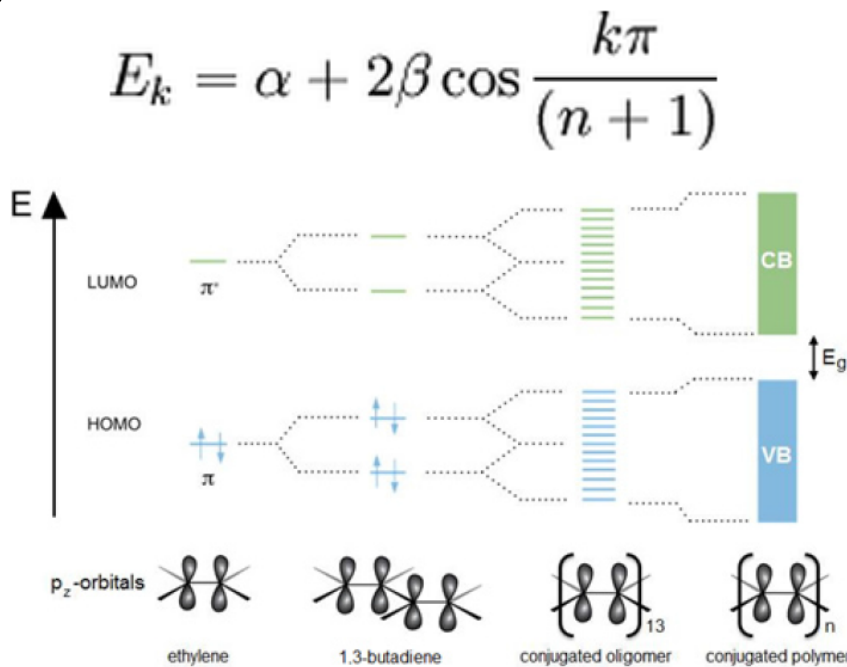
Monomer HOMO/LUMO leads to continuous valence (VB) and conduction bands (CB) in conjugated systems

HOMO: Highest occupied molecular orbital (valence band)
LUMO: Lowest unoccupied molecular orbital (conduction band)

Origin of Band Gap in Conjugated Polymers

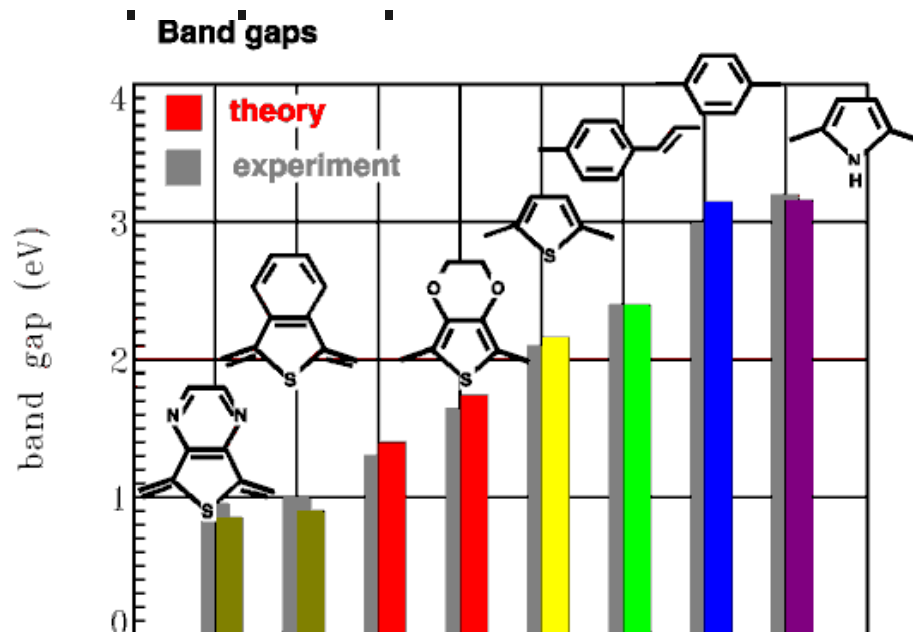
Energy level splitting (Hückel model):

- Molecular orbital treated as a linear combination of atomic (pi) orbitals.



Band Gap tuning

Because the band gap energy, E_g , depends on the molecular structure of the repeat unit, optical and electronic properties can be controlled at the mol



Structure-Properties of Conductive Polymers

Polymer (date conductivity discovered)	Structure	•••* gap (eV)	Conductivity [#] (S/cm)
I. Polyacetylene and analogues			
Polyacetylene (1977)		1.5	$10^3 - 1.7 \times 10^5$
Polypyrrole (1979)		3.1	$10^2 - 7.5 \times 10^3$
Polythiophene (1981)		2.0	$10 - 10^3$
II. Polyphenylene and analogues			
Poly(paraphenylene) (1979)		3.0	$10^2 - 10^3$
Poly(p-phenylene vinylene) (1979)		2.5	$3 - 5 \times 10^3$
Polyaniline (1980)		3.2	30 - 200

Note the alternating single-double bond structure.

Visible spectrum: 1.7eV - 3.1eV



Band gaps tunable for PV/LED applications

[#] The range of conductivities listed is from that originally found to the highest values obtained to date (after Dai, 1999, copyright 1999 Marcel Dekker, Inc.)

Insights into Solid State Physics

Peierls Transition

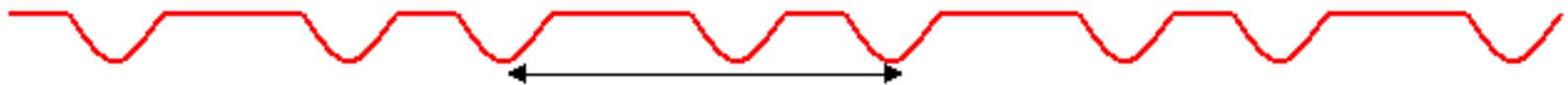
Peierls' Theorem states that:

a one-dimensional equally spaced chain with one electron per ion is unstable.

Peierls Transition: At low temperatures, 1D crystals show insulating behavior. Why?

- Atoms in the lattice rearrange slightly to minimize total energy.

Total system length $L = Na$ (as before) for N ions



System now has longer period: $2a$

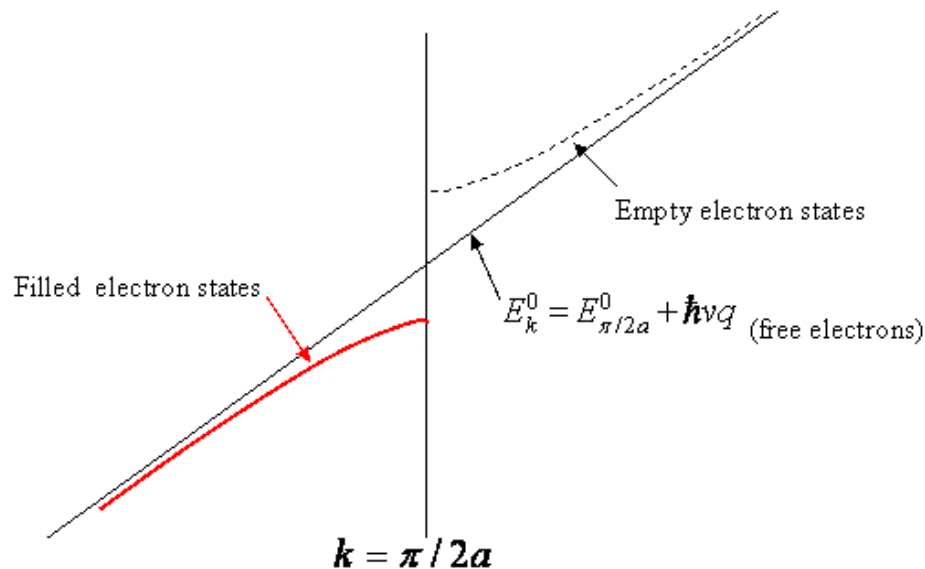
(Similar to Kronig-Penney model)

The result is **dimerization** - effective period of $2a$ instead of a .

(The reason for this is an example of applied second-order perturbation theory)

Peierls Transition

Energy landscape in k space across repeat unit in dimerized material



If the electrons fill all the states to $|k| = \pi/2a$ and none beyond (as for monovalent atoms at low T), then the opening of a gap at $|k| = \pi/2a$ means that ***all the electrons are in states whose energy is lowered.***

Change in electronic energy levels near $k = \pi/2a$ from dimerization: in this region, the free electron curve is approximated with a straight line: $q = k - \pi/2a$.

Insulator-Metallic Transition

- Conductive polymers are insulators in pure form.
- Dopants must be added for I-M transition to occur.
 - Dopant atoms or molecules are inserted between polymer chains rather than replacing host atoms.
 - Dopants either oxidize to create a positive charge or reduce to create a negative charge on the chain.
 - Disorder, interchain interaction, and doping level determine the insulator-metal transition in conducting polymers

Insulator-Metallic Transition

How is I-M transition determined experimentally?

- Reflectivity data gives complex dielectric constant, ϵ
- According to Drude Model,

$$\epsilon_1 = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad \Omega_p^2 = \frac{\omega_p^2}{\epsilon_\infty} - \gamma^2$$

$$\sigma_{\text{Drude}}(\omega) = \frac{1}{4\pi} \frac{\Omega_p^2 \tau}{1 - i\omega\tau}$$

where $\omega_p^2 = 4\pi e^2 N/Vm^*$

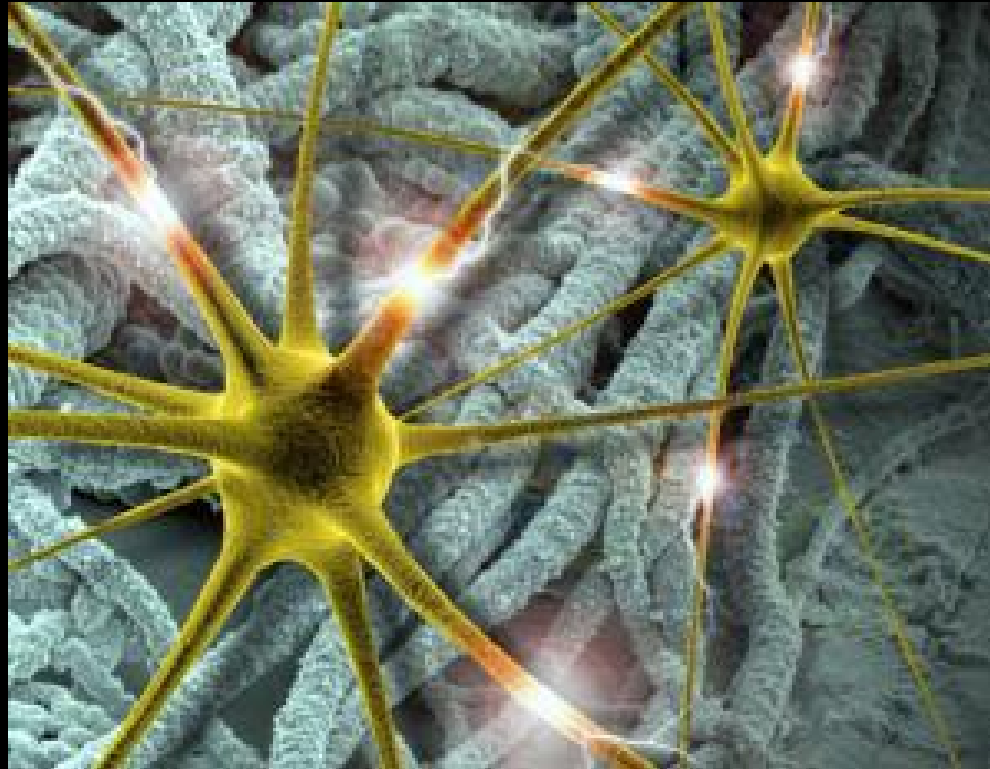
is the unscreened plasma frequency, N/V is the free carrier concentration, $\epsilon(\text{inf})$ is the high-frequency dielectric constant, and m^* the effective mass of the charge carriers

$\gamma = 1/\tau$ = inverse relaxation time

Better model for samples containing disorder - localization modified Drude Model:

$$\sigma_{\text{LMD}}(\omega) = \sigma_D(\omega) \left\{ 1 - \frac{C}{(k_F \lambda)^2} \left[1 - \left(\frac{3\omega}{\gamma} \right)^{1/2} \right] \right\} \quad \text{where } \sigma_D(\omega) = \frac{\omega_p^2 \gamma}{4\pi(\omega^2 + \gamma^2)}$$

New Horizons



<http://www.sciencedaily.com/releases/2009/09/090929181818.htm> "Step Toward Better Brain Implants Using Conducting Polymer Nanotubes"

Future Applications?

- Applications of polymers for thermoelectrics? (low thermal, high electrical conductivity materials)
- Biosensors and medical devices
- Biocompatible electrodes
- Solid-state electrode batteries?

Theory and Fundamental Questions?

- Better understanding of the role of conjugation length, interchain transport, and crystallinity in charge transport properties
- How to prevent degradation?
- High performance materials while maintaining processability?

Questions?



Origin of Band Gap in Conjugated Polymers

Energy level splitting (Hückel model), butadiene example:

In the Hückel treatment for butadiene, the MO Ψ is a linear combination of the 4p ϕ AO's at carbon with their ratios c :

$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$

The secular equation is:

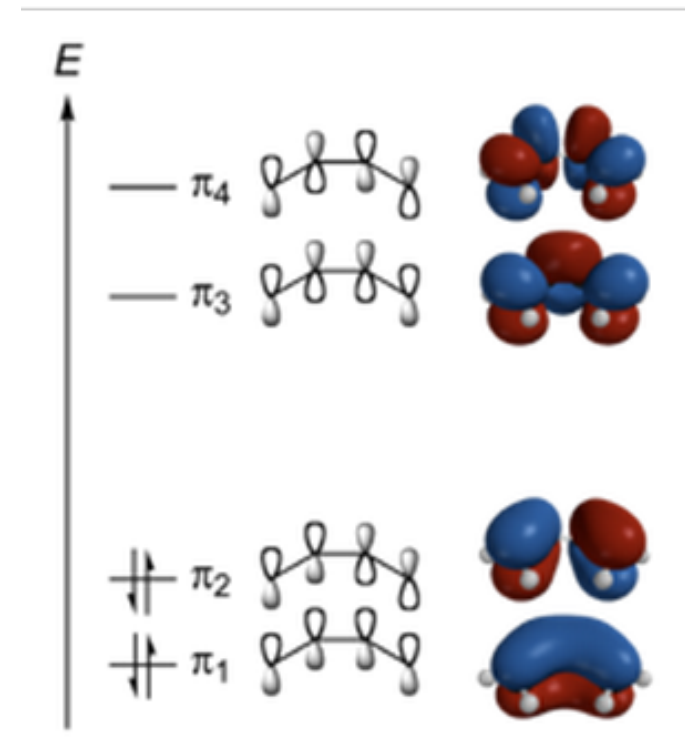
$$\begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0$$

which leads to

$$(\alpha - E)(\alpha + \beta - E) - \beta^2 = 0$$

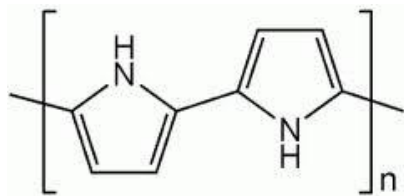
and:

$$E_{\pm} = \alpha + \frac{1 \pm \sqrt{5}}{2} \beta$$

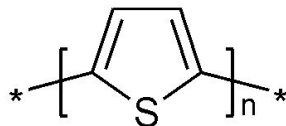


Some Common Conductive Polymers....

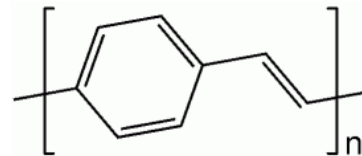
- POLYACETYLENE - Our first conductive polymer!
- 1980s - other polymers studied, including polypyrrole, polythiophene (and derivatives), polyphenylenevinylene and polyaniline.



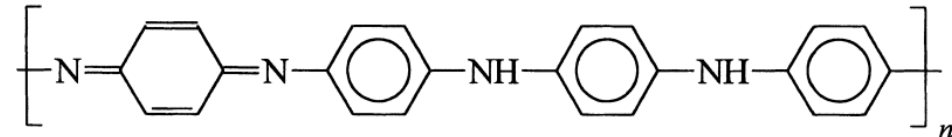
polypyrrole



polythiophene



polyphenylenevinylene



polyaniline

Notice that they all have alternating double-single carbon bonds!

- More recent: Poly(ethylenedioxythiophene) (PEDOT)

*Some chemists will argue that it should be called poly(vinylene). Potato, potahto.