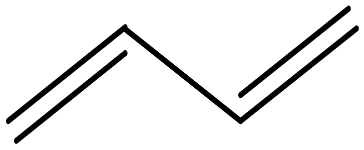
Materials Chemistry III
Day 8

Day 8

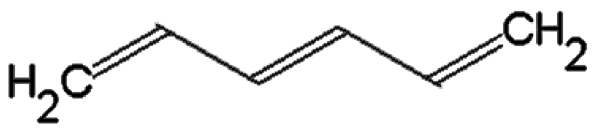
1) Sp^2 hybridiztion, conjugated systems and energy transition energy calculation-conjugated polymer system.
2) Electronic transition energy calculation.
3) Concept of Particle in a Ring!
4) Conjugated polymer system and their band gap.
5) Optical property measurement using UV-Visible absorbance spectroscopy, Lambert beers law.

For Electronic Transition in Conjugated System

Ethylene



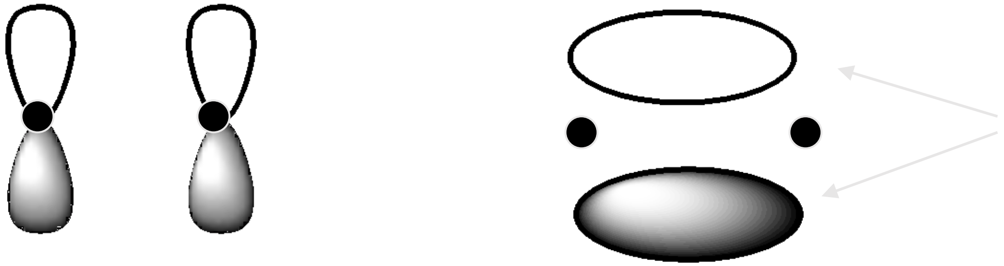
Butadiene



Hexatriene

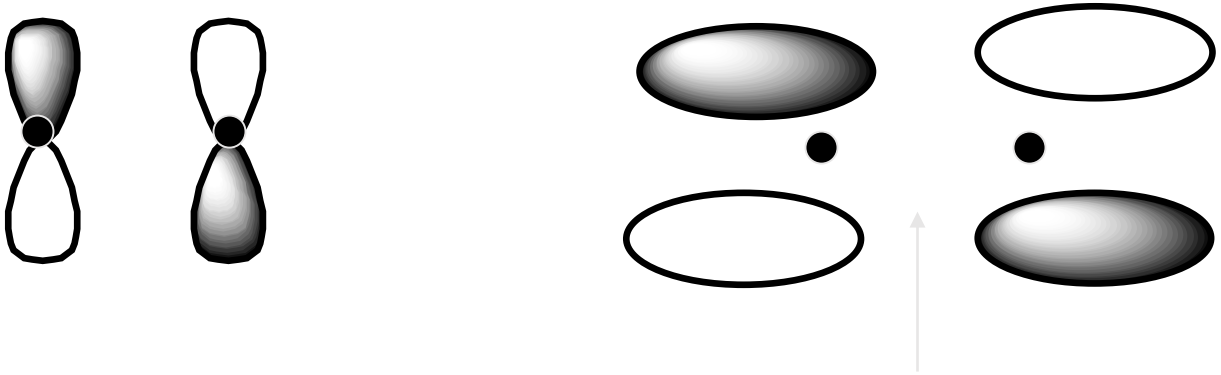
π bonds

Bonding combination of p orbitals (π)



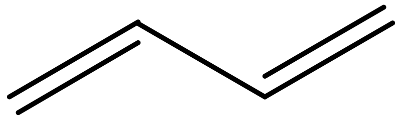
electron density builds up between the nuclei

Antibonding combination of p orbitals (π*)



The wavefunctions cancel between the nuclei.

Butadiene



butadiene

n=2

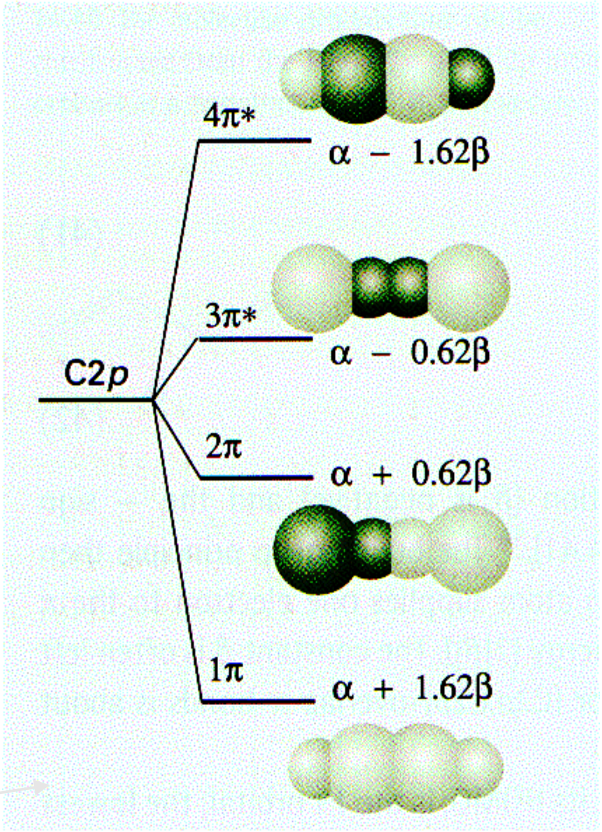
To generate the molecular orbitals of larger molecules, we take linear combinations of the atomic orbitals from each atom. If there are n atoms, there will be n different combinations.

fully antibonding

partially antibonding

partially bonding

fully bonding



3 nodes

2 nodes

1 node

0 nodes

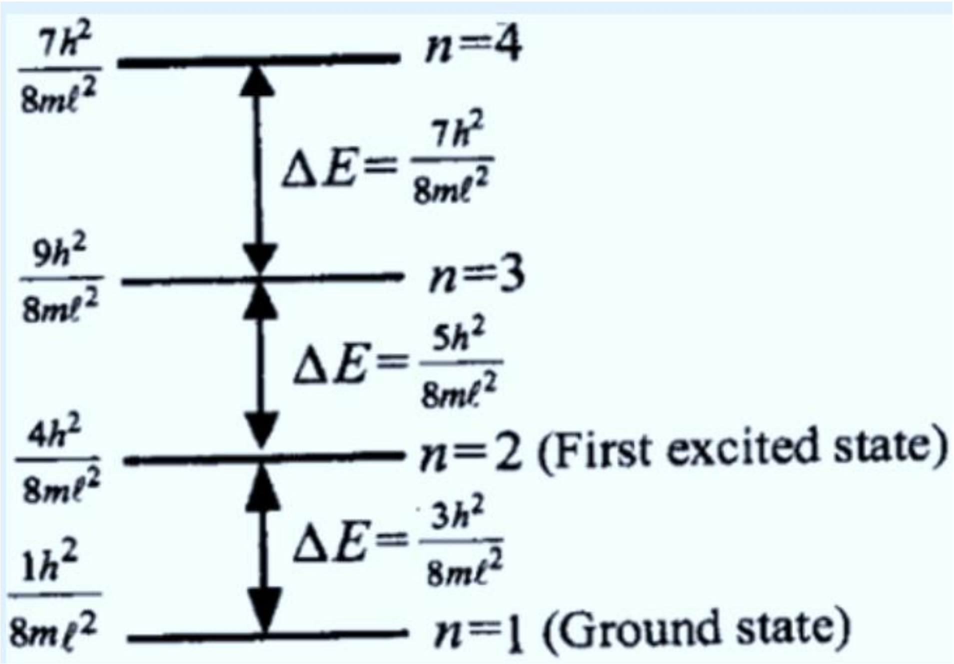
Atkins, *Physical Chemistry*

An important application of particle in a 1D box is in explaining the color of conjugated systems. The π-electrons in polyene behaves similar to the system of particle in 1D box. The π-electrons are distributed by following Pauli exclusion principle and Aufbau principle.

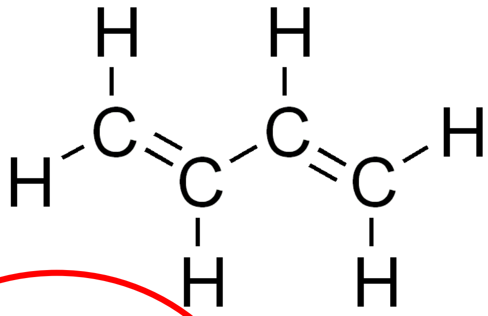
n=(number of π-electrons/2)

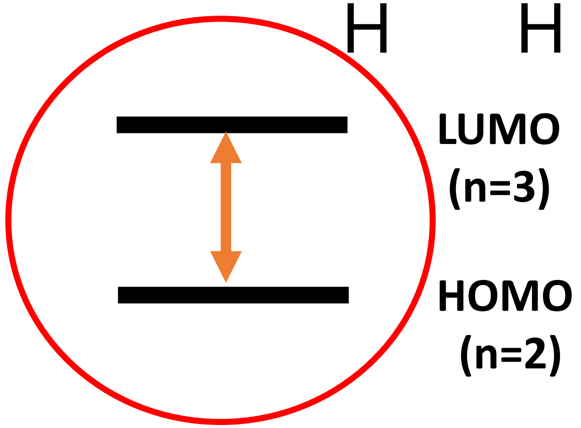
$$E=n^2h^2/8mL^2$$

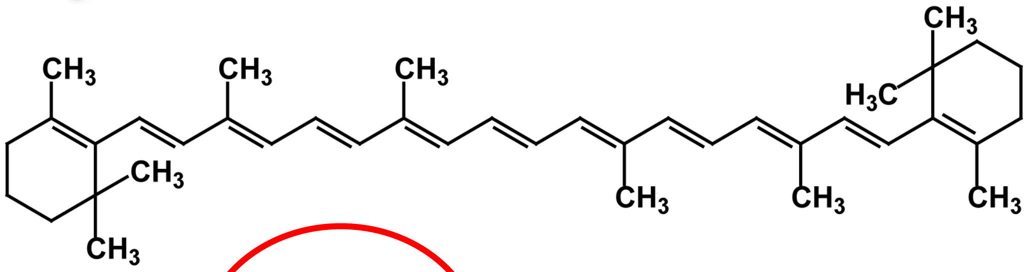
For Electronic Transition in Conjugated System

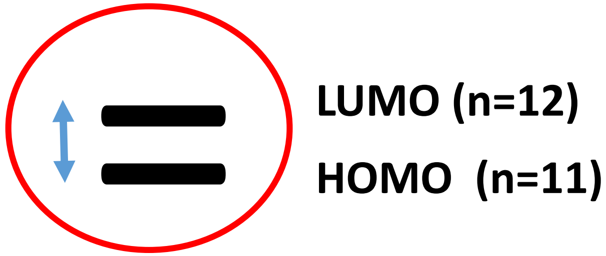


Extrapolation



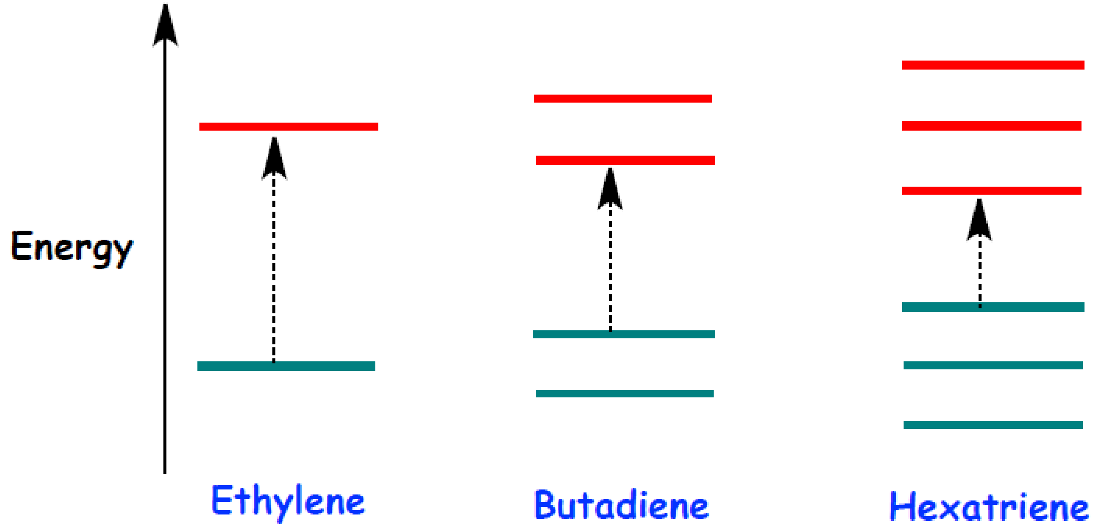






The trend in color shift can be explained!

Effect of Conjugation



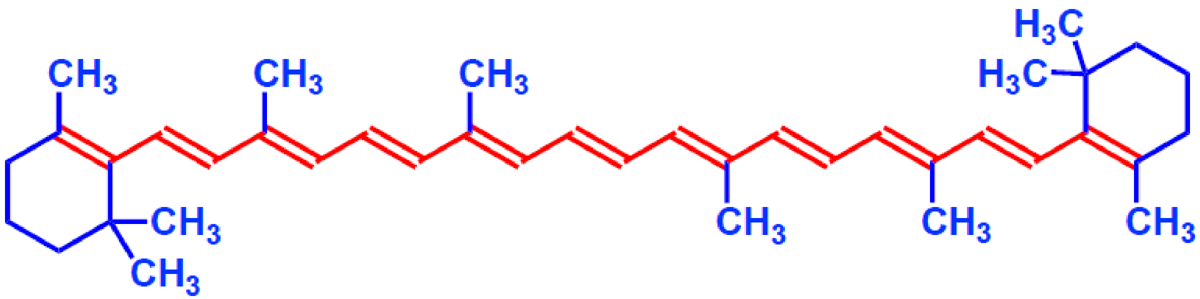
Compare 1D box?

Molecule	λ_{max} (nm)
Ethylene	165
1,3-butadiene	217
1,3,5-hexatriene	258
β-Carotene	470

Calculated (1D box model)

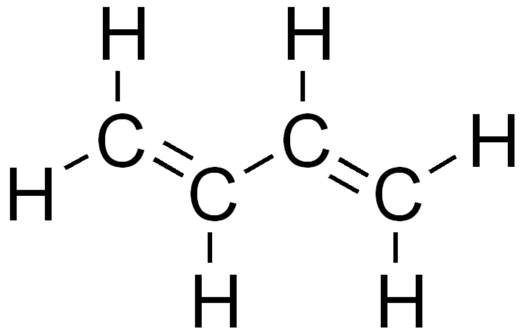
220 nm (for 1,3 butadiene)

1370 nm (for 1,3 butadiene)



Spectrum?

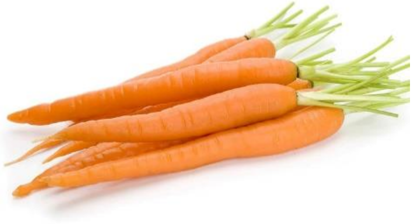
n=2



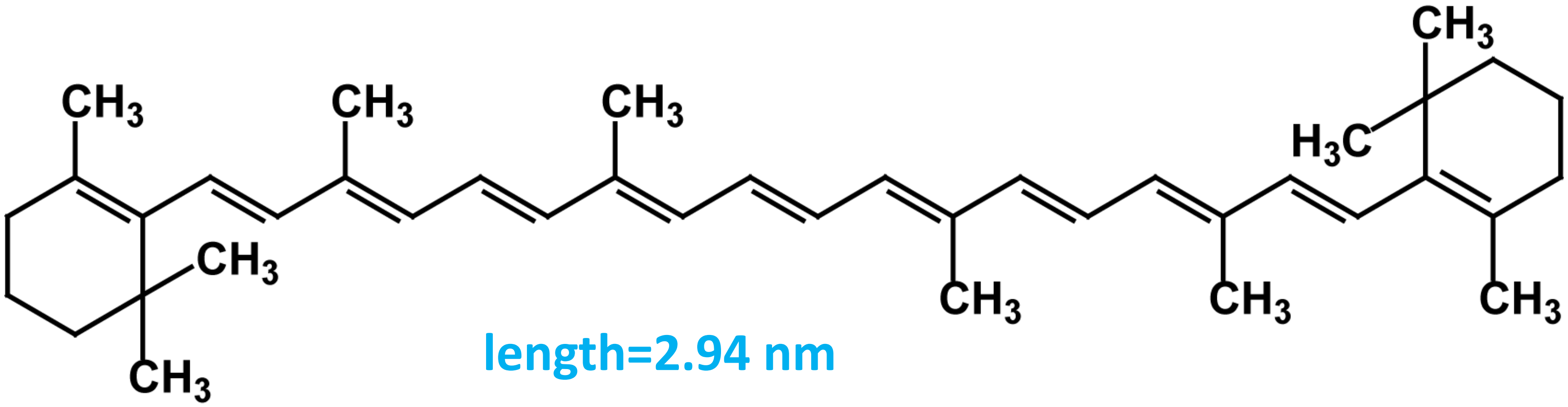
Butadiene; $\Delta E = 9.02 \times 10^{-19}$ J

length=0.578 nm

VS



n=11



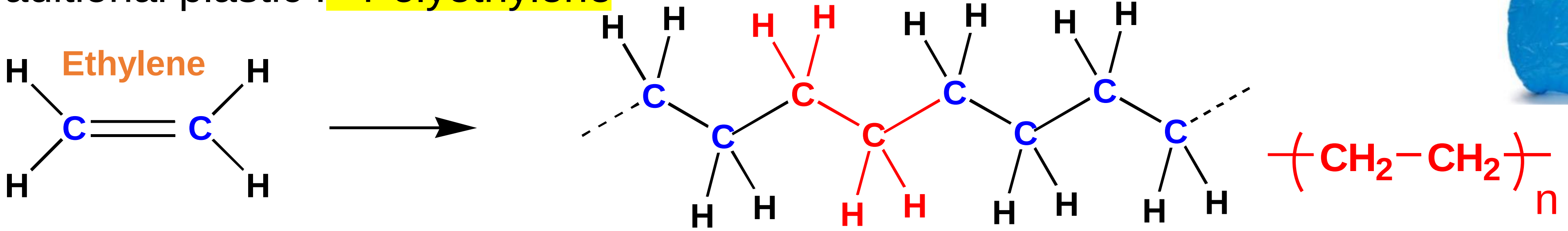
length=2.94 nm

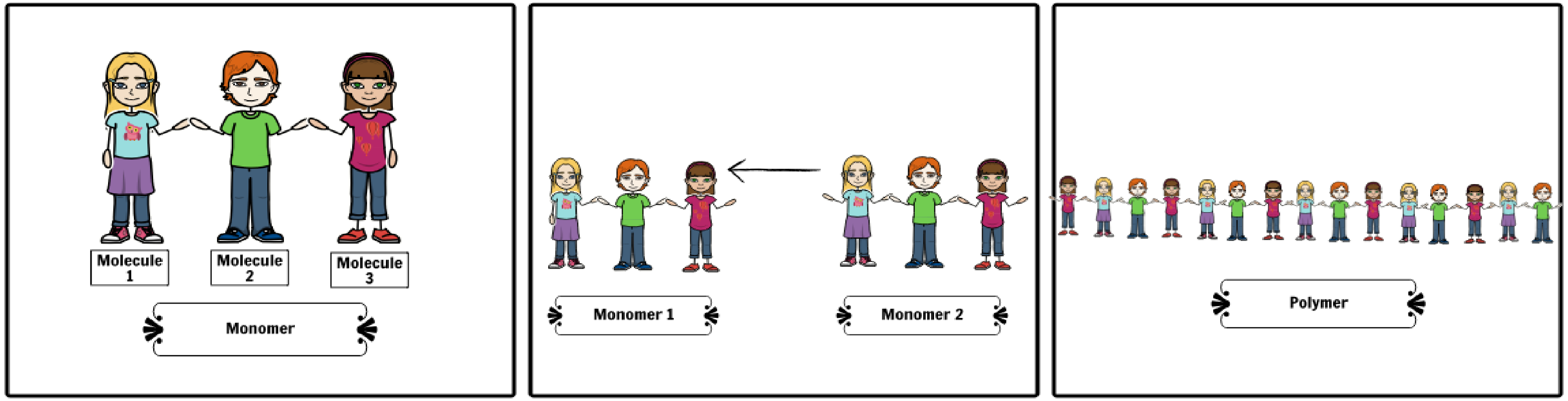
β-carotene-extended conjugated system **$\Delta E = 1.6 \times 10^{-19}$ J**

- **To compute the absorption wavelength, we need the following data:**
- **Butadiene, length = 0.578 nm.**
- **β-carotene, length=2.94 nm.**
- **m_e= 9.109×10^{-31} kg, h = 6.626×10^{-34} J-s**
- **C = 2.99×10^{8} m s^{-1}**

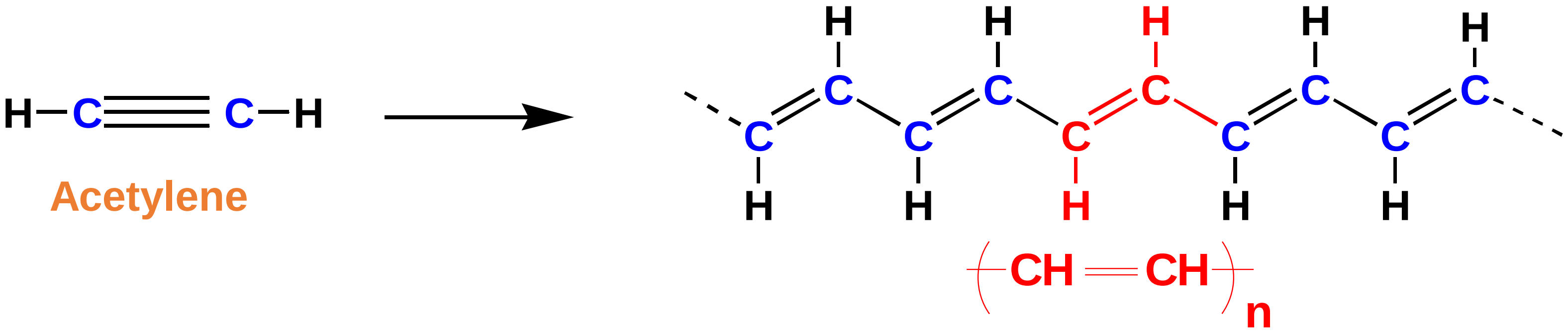
Conjugated Polymers-Plastic solar cells

- Traditional plastic : Polyethylene

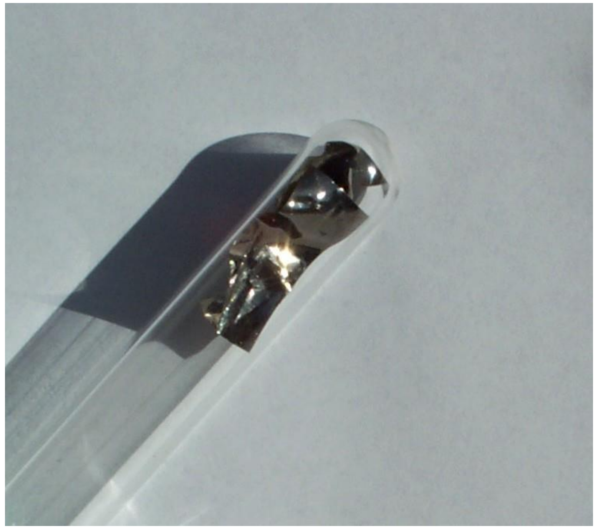


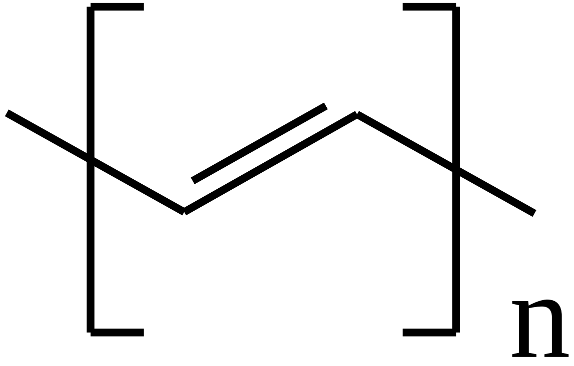


- Conjugated polymer : Trans-polyacetylene



Conjugated Polymers





Trans-polyacetylene (t-PA)

Applications

OLED

OFET

OPV

How do we explain the band properties of large conjugated system?

Nobel Prize in Chemistry 2000

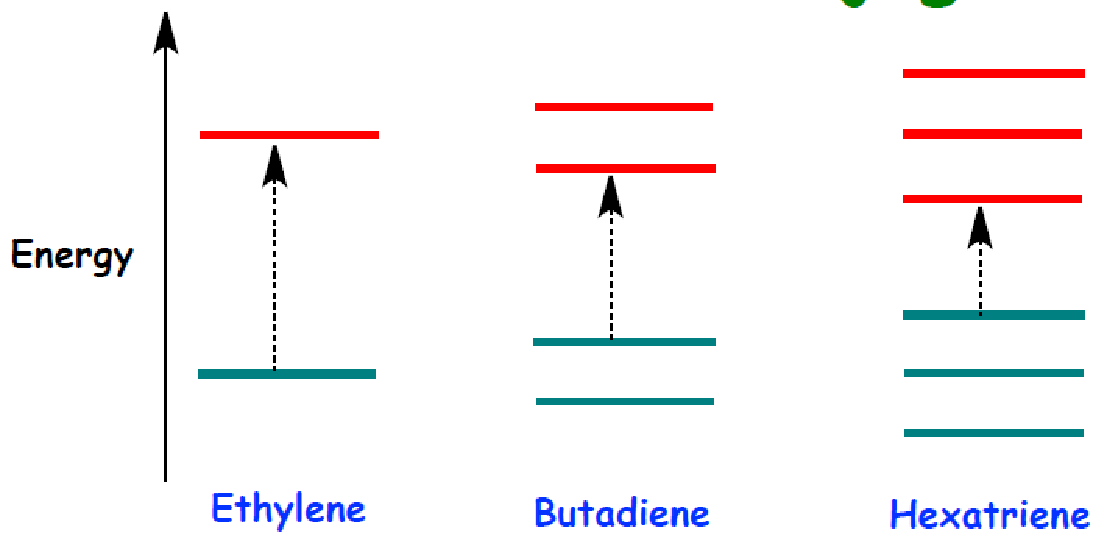
"For the Discovery and Development of Conductive Polymers"

Hideki Shirakawa
University of Tsukuba

Alan Heeger
University of California at Santa Barbara

Alan MacDiarmid
University of Pennsylvania

Effect of Conjugation



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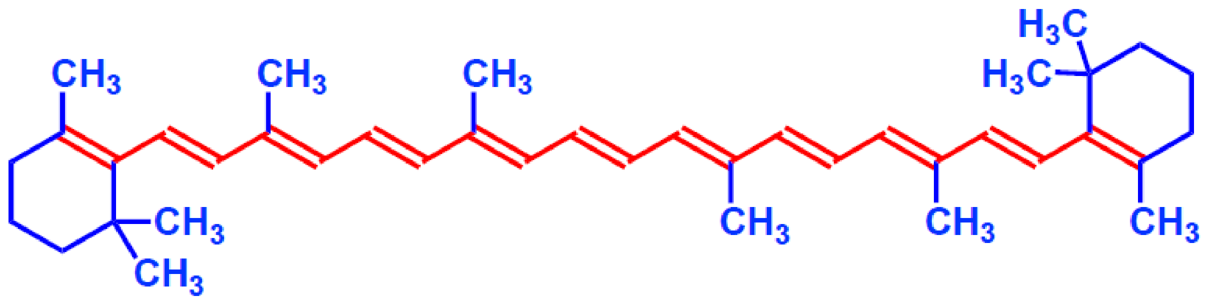


Spectrum?

Why deviation?

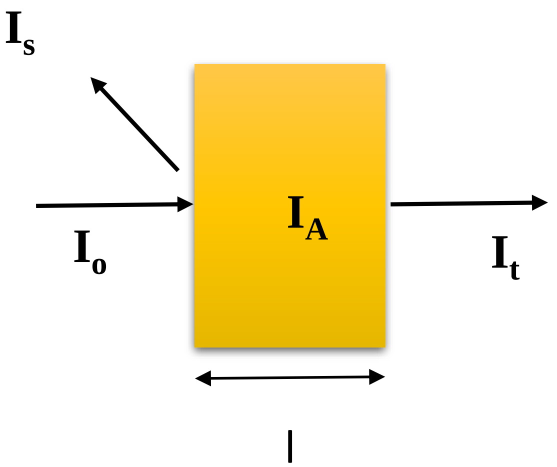
- **Effect of solvent!**
- **Chain rotation!**
- **1D Box model is a crude model, which provides the trend!**

UV-Visible spectroscopy-Measurement of Electronic Transition Electron-Mater Interaction!

Lambert-Beers law

When a monochromatic radiation is passed through an absorbing medium a part of the incident radiation is scattered by the absorbing medium, a part is absorbed and rest of which is transmitted.

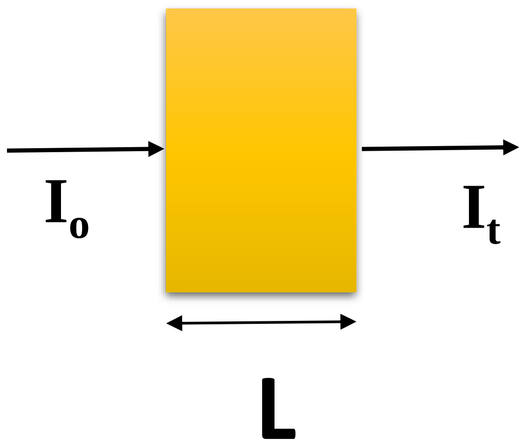
Scattering effect may be minimized by using a specific geometry of the sample holder/cuvette.



$$I_o = I_t + I_s + I_A$$

Lambert's law

When a monochromatic radiation is passed through a medium, the decrease in intensity of the radiation w.r.t the length of the absorbing medium is proportional to the intensity of the radiation.



$$-[dI/dL] \propto I$$

$$\log(I_t/I_o) = -ZL$$

Where Z is the extinction co-efficient.