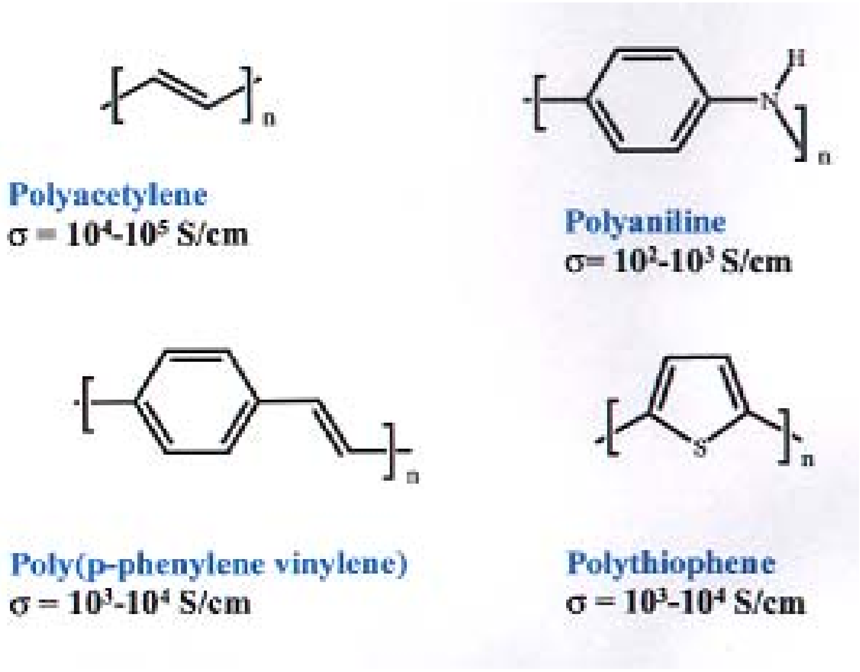
Electronic Polymers

Insulators	Semiconductors	Metals	Superconductors
$\sigma < 10^{-7}$	$10^{-7} < \sigma < 10^{2}$	$\sigma > 10^{2}$	$\sigma >> 10^{20}$



σ ranges 10^{-20} to 10^{20}

Requires doping (oxidation or reduction) for conductivity

Electrical Properties

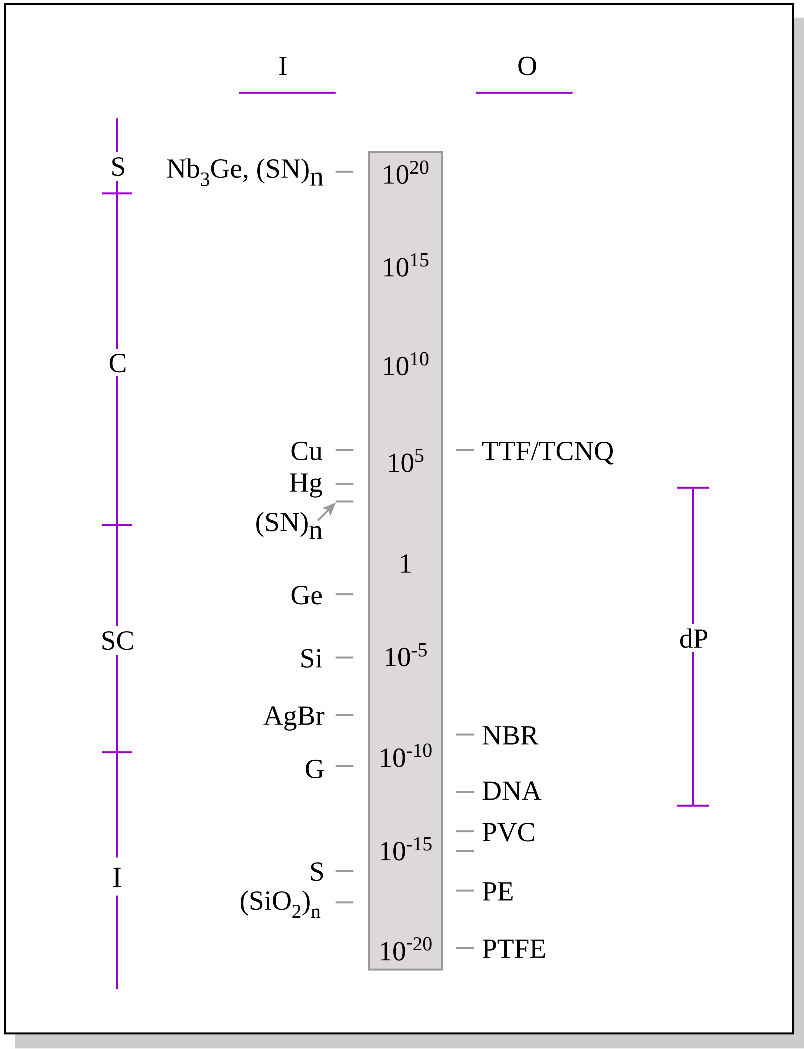


Figure by MIT OCW.

Electric conductivity of inorganic (I) and organic (O) compounds, measured in S/cm. Triniobium germanide (Nb_3Ge) and poly(thiazyl) $(SN)_n$ are superconducting materials at very low temperatures near zero kelvin. The conductivities for conducting (C), semi-conducting (SC) and insulating (I) compounds are given for 20°C (= 293.16 K = 68°F). Cu = Copper, Hg = mercury, Ge = germanium, Si = silicon, AgBr = silver bromide, G = glass, S = sulfur, $(SiO_2)_n$= quartz, TTF = tetrathiafulvalene, TCNQ = 7,7,8,8 tetracyanoquinodimethane, NBR = nitrile rubber (a copolymer from acrylonitrile and butadiene), DNA = deoxyribonucleic acid, PVC = polyvinyl chloride, PE = polyethylene, PTFE = polytetrafluoroethylene.

1 Siemens = 1 Ohm^{-1}

10^{40} change in material property !

Material	Conductivity (S/cm)
Insulators	$\sigma < 10^{-7}$
Semiconductors	$10^{-7} < \sigma < 10^{2}$
Metals	$\sigma > 10^{2}$
Superconductors	$\sigma >> 10^{20}$

$$\sigma = n\mu q$$

n = # carriers/cm^3

μ= mobility (cm^2/V•sec)

q = charge

Types of Charge

- Usual carriers: electrons, holes, ions(cations & anions)
- New for conducting polymers – solitons, polarons, bipolarons

$$J_i = \sigma_{ij} E_j$$

where J_i is the current, σ_{ij} is the conductivity and E_j is the applied field

<u>Battery Application</u>

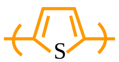
- **Li-polymer** vs Pb.
- Weight: 1/10th
- volume: 1/3rd
- power density: 10x
- processable into any shape; dry, no toxic fumes etc.

Examples of Conducting Organic Polymers & Dopants

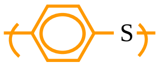
Polyacetylene
(I_2, Br_2, Li, Na, AsF_5)
10^4 - 10^5 S/cm

Poly (p-phenylene)
(Li, K, AsF_5)
10^2 - 10^3 S/cm

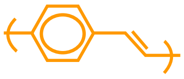
Polyaniline
(HCl, R-SO_3H)
1- 400 S/cm



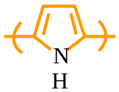
Polythiophene
($FeCl_3$, $NOPF_6$, BF_3)
10- 10^3 S/cm



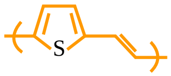
Poly (p-phenylene sulfide)
(AsF_5)
100 - 500 S/cm



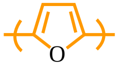
Poly (p-phenylene vinylene)
(AsF_5)
10^2 - 10^4 S/cm



Polypyrrole
($FeCl_3$, BF_3)
10_2 - 10_3 S/cm



Poly (thienylene vinylene)
(AsF_5)
10 - 10^3 S/cm



Polyfuran
(BF_3)
1 - 100 S/cm

Figure by MIT OCW.

Electrifying Plastics

Nobel Prize in Chemistry honors three who pioneered a new materials field

Prof. Alan J. Heeger,64
Physics and Materials Science
UCSB

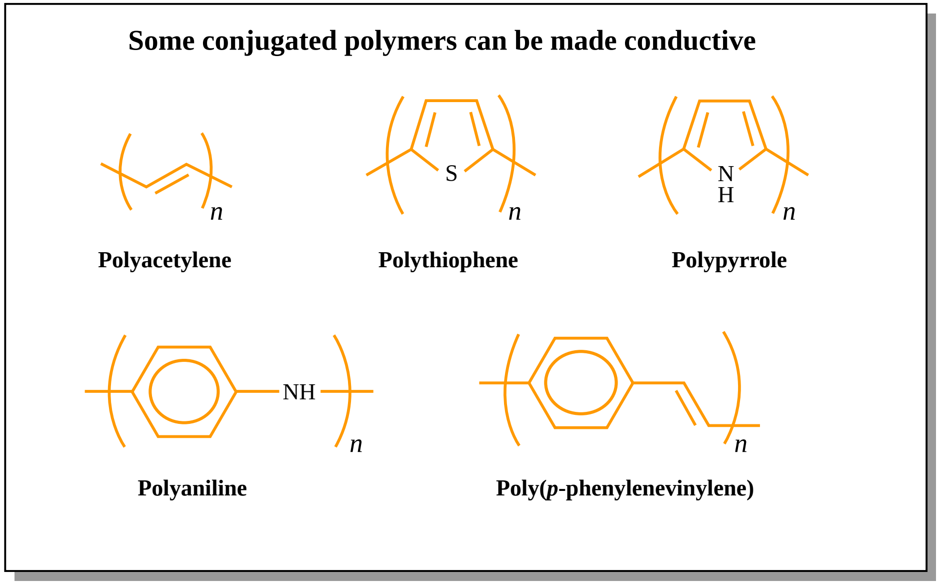


Figure by MIT OCW.

Prof. Hideki Shirakawa, 64
Univ. of Tsukuba, Japan (ret.)

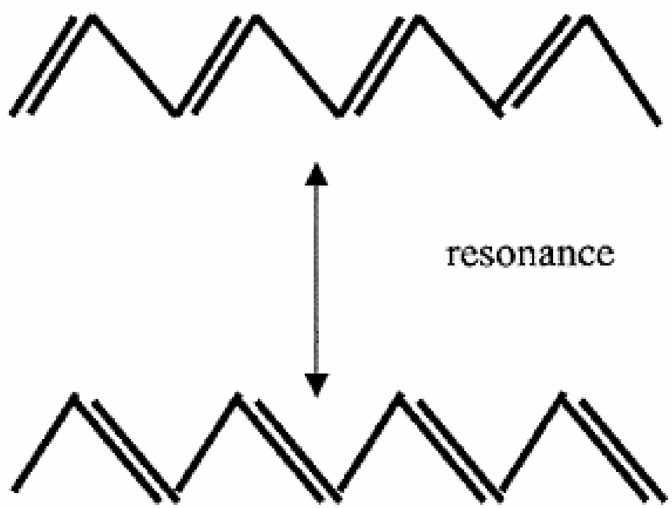
Prof. Alan G. MacDiarmid, 73
Chemistry, Univ. of Pennsylvania

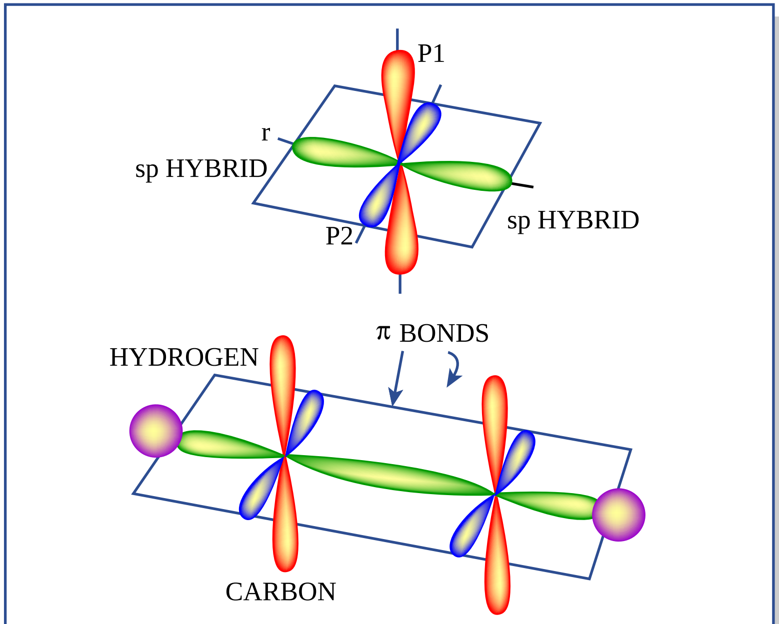
How to Make a Conducting Polymer (Polyacetylene)

(2000 Nobel Prize in Chemistry)

Heeger, MacDiarmid, Shirakawa

Create chemical structures with delocalized electrons: extended π bonding.
e.g. conjugated double bonds alternating with single bonds as in $-(CH{=}CH)_x-$.





Bonding in acetylene H-C=C-H

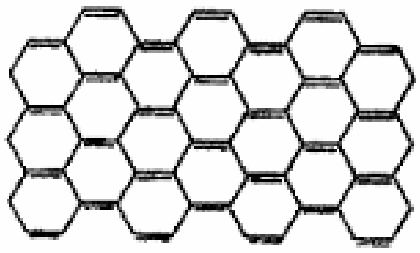
acetylene

Figure by MIT OCW.

Conducting Polymers

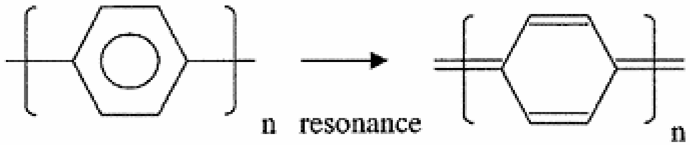
graphite (sp² bonding)   a sort of "polymerized benzene"

$\sigma_{\parallel} \cong 10^5$ S/cm
$\sigma_{\perp} \cong 10^1$ S/cm



Graphite

poly (paraphenylene) "PPP"



Conducting polymers also exhibiting graphite lattice structure:

- poly(p-phenylene)
- cis-poly(acetylene)
- trans-poly(acetylene)

Polyacetylene

Polyacetylene—anticipate a 1-d metallic conductor from π-bonds with delocalized electrons.

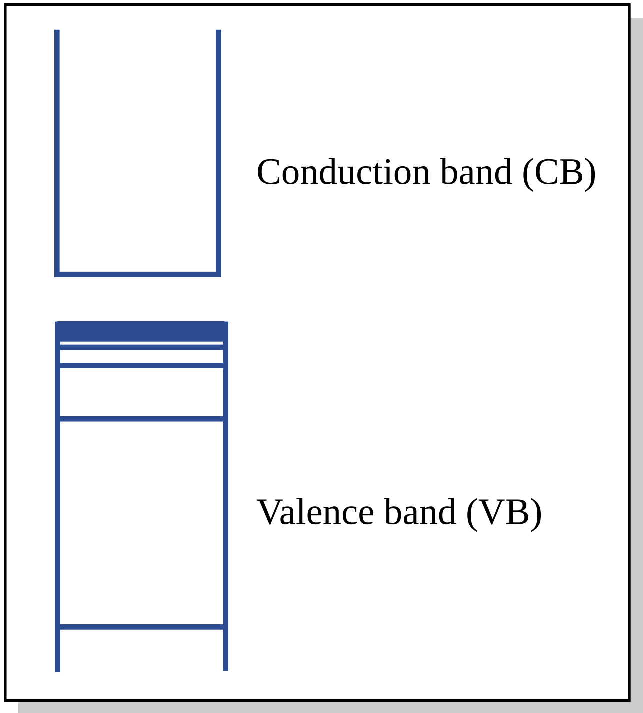


Figure by MIT OCW.

but instead find $\sigma \cong 10^{-9}$ S/cm

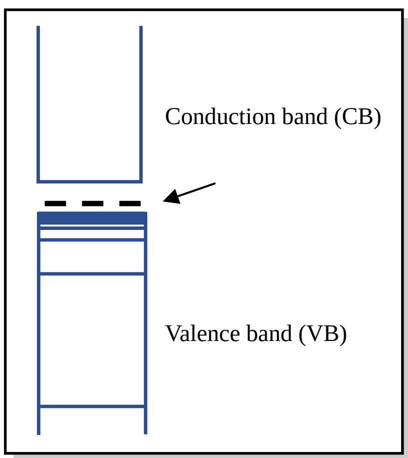
$E_{gap} \cong 1.5$ eV

The reason polyactylene is a insulator is that bond alteration occurs: due to Peierls stress induced

$$\cdots = - = - \cdots$$

Doped Polyacetylene

Dope (oxidation of VB electron)
To create a conductor, one can dope polyacetylene with AsF_5 which oxidizes the VB electrons of polyactylene and creates conduction via p-type transport



$\sigma \cong 500$ S/cm

10^{-9} to 10^{-2}

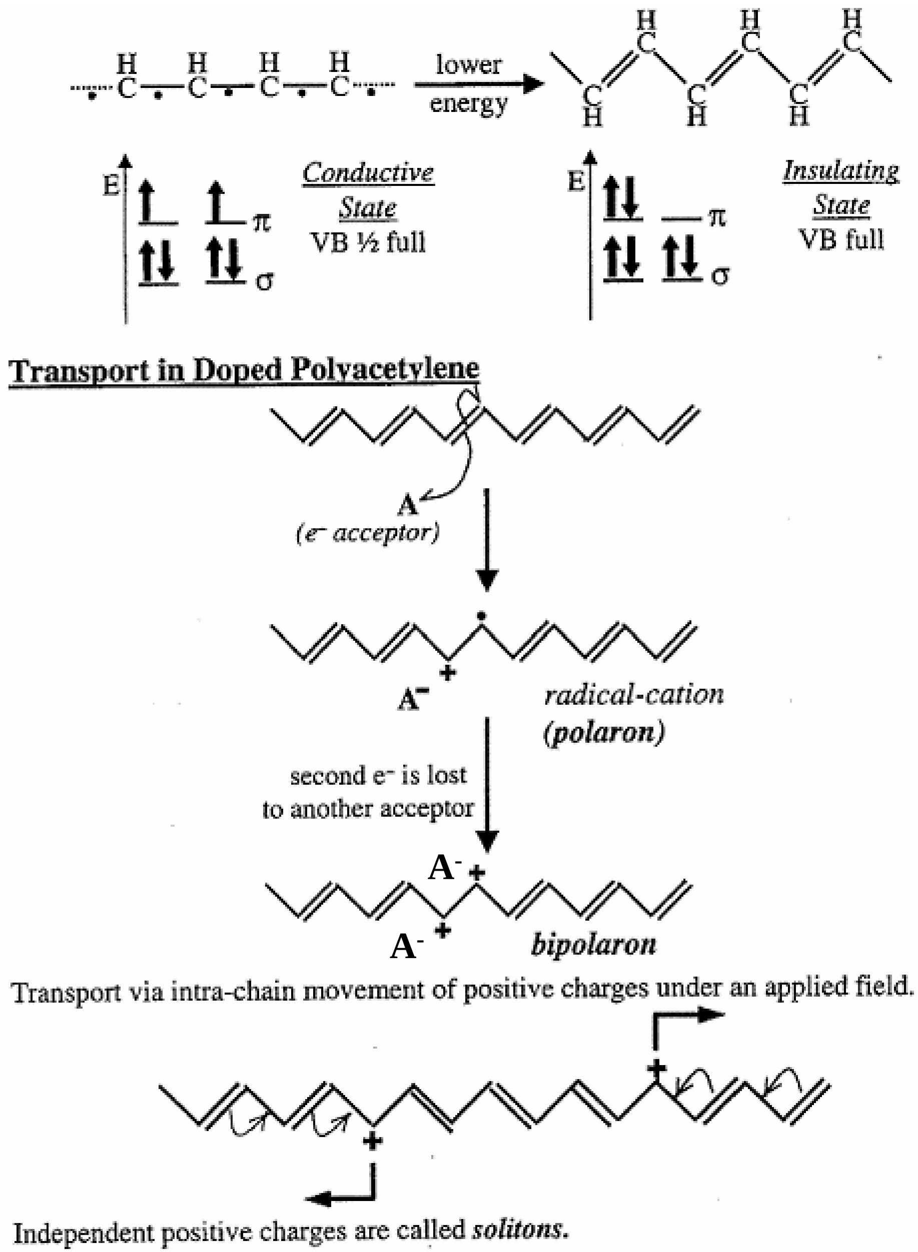
Figure by MIT OCW.

Mobility of charge carriers in doped conjugated polymers depends on:

(1) chain conformation (intra-chain hoping)
(2) chain packing (inter-chain hoping)
(3) crystal size/orientation (inter-grain hoping)

Peierls Transition

Pick basis of
6 electrons
Per C_2H_2



Light Emitting Polymers

Photoluminescent and Electroluminescent

Image and text removed due to copyright restrictions.

Please see Fig. 1 in Kraft, Arno, et al. "Electroluminescent Conjugated Polymers – Seeing Polymers in a New Light." *Angewandte Chemie International Edition* 37 (1998): 402-428.

Polymers for LEDs

Images and text removed due to copyright restrictions.

Please see Fig. 3 and Table 2 in Kraft, Arno, et al. "Electroluminescent Conjugated Polymers – Seeing Polymers in a New Light." *Angewandte Chemie International Edition* 37 (1998): 402-428.

Light-emitting BCP/CdSe

- Electrons and holes trap on dots, recombine, and radiate visible light.

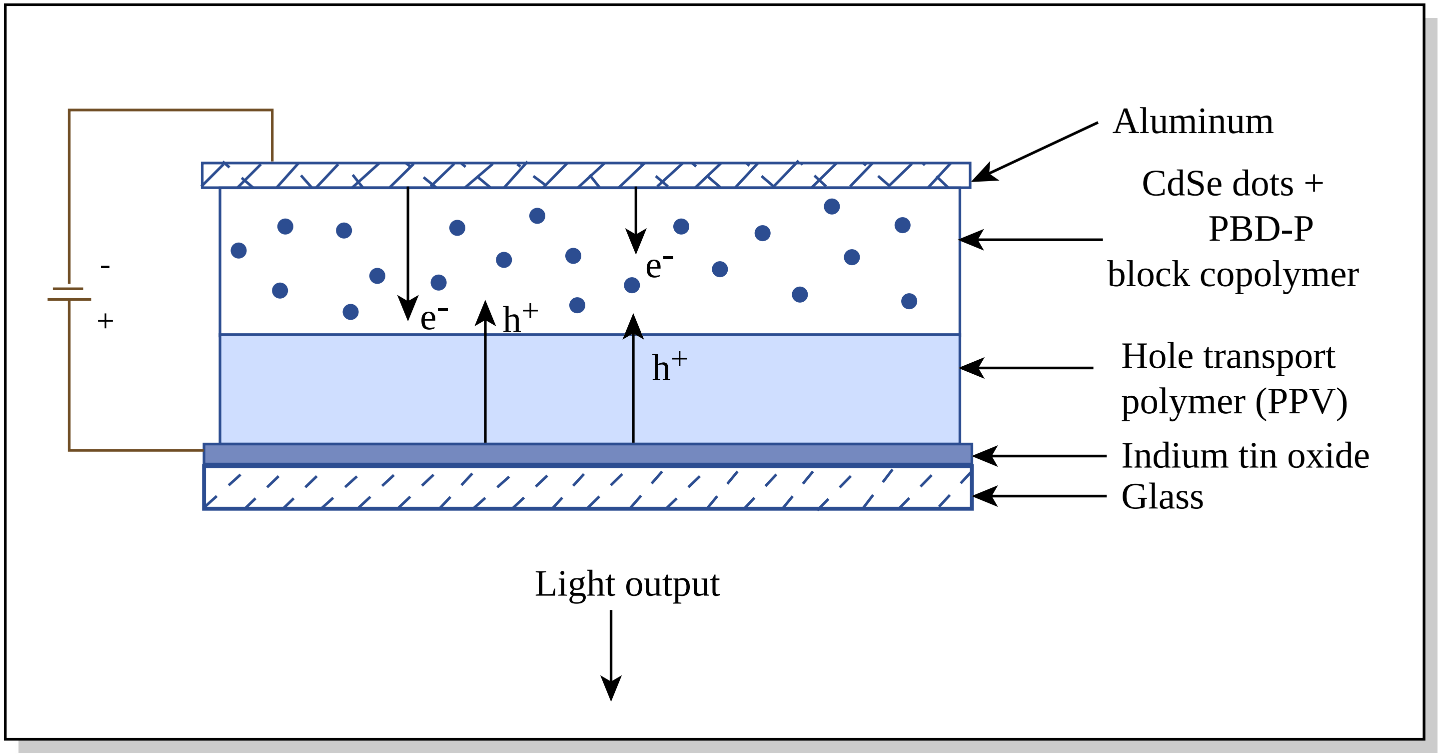


Figure by MIT OCW.

- How does block copolymer/quantum dot morphology affect confinement and recombination?

- Polyphenylenevinylene (PPV) layer blocks electrons, confining recombination of electrons and holes away from ITO electrode.

CdSe Nanoparticles Targeted into Hole Transport Block

CdSe

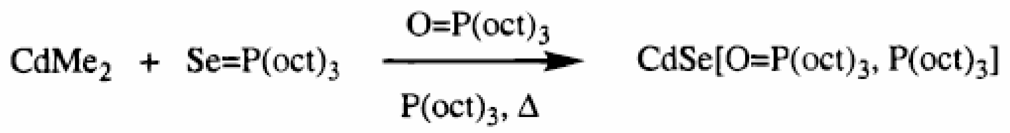
Image removed due to copyright restriction.

Please see Fig. 6 in Fogg, D. E., et al. “Fabrication of Quantum Dot/Polymer Composites: Phosphine-Functionalized Block Copolymers as Passivating Hosts for Cadmium Selenide Nanoclusters.” *Macromolecules* 30 (1997): 417-426.

CdSe +

$((NBE\text{-}CH_2O(CH_2)_5P(oct)_2)\text{-}b\text{-}MTD)$

Electroluminescence in PPV/CdSe Hybrid



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Please see Fig. 6 in Matoussi, H. et al. “Composite Thin Films of CdSeNanocrystals and a Surface Passivating/Electron Transporting Block Copolymer: Correlations Between Film Microstructure by Transmission Electron Microscopy and Electroluminescence.” *Journal of Applied Physics* 86 (October 15, 1999): 4390-4399.

"Artificial Muscle Materials"

- Move robots
- Assist weak/damaged muscle
- Improve natural capabilities
- Direct biomedical devices

Images removed due to copyright restrictions.

Please see
http://bleex.me.berkeley.edu/bleex.htm
http://www.rf-ablation.engr.wisc.edu/pix/cardiac_catheter_placement.jpg
http://world.honda.com/ASIMO/

Must Be:
- Quiet
- Lightweight
- Flexible
- Powerful
- Low energy
- Inexpensive

Why is natural muscle so good?

- Large strains (20-40%) and strain rates (>50%/sec)
- Control of stiffness
- Silent Operation
- High energy density
- Integrated fuel delivery, heat and waste removal
- Operation for billion of cycles

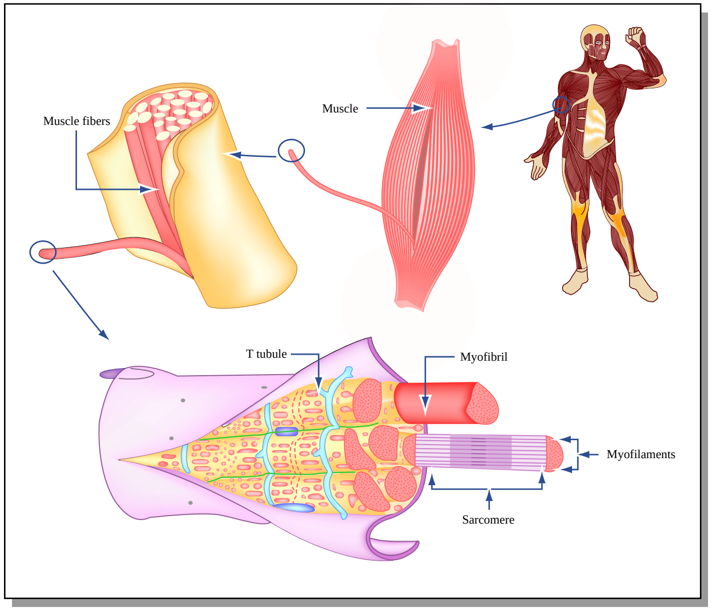


Figure by MIT OCW.

extended

contracted

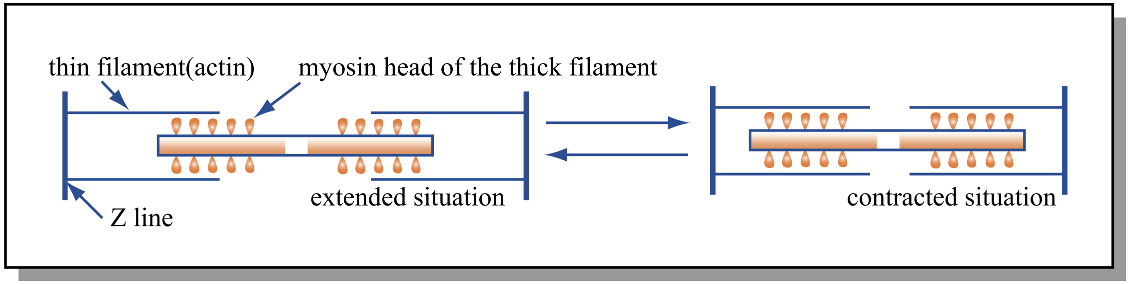


Figure by MIT OCW.

How can we do this synthetically ?

Try to mimic nanoscale mechanism

- Hard to make the individual parts (synthesis)
- Hard to put them together in the right way (processing)

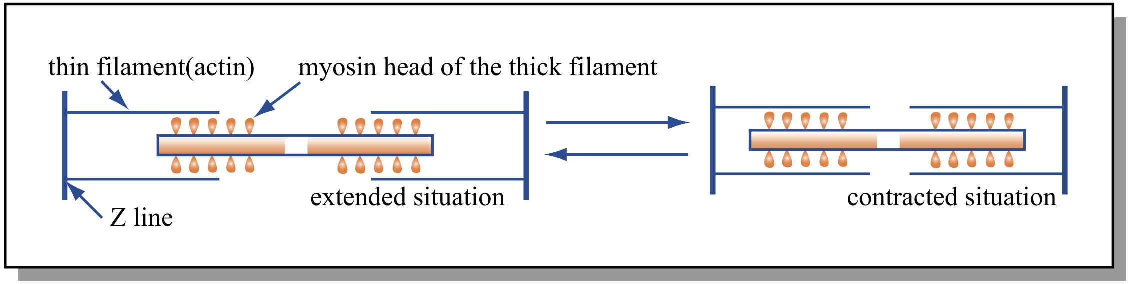


Figure by MIT OpenCourseWare.

Image removed due to copyright restriction.

Please see Fig. 8 in Collin, Jean-Paul, et al. “Shuttles and Muscles: Linear Molecular Machines Based on Transition Metals.” *Accounts of Chemical Research* 34 (2001): 477-487.

Current Actuator Materials

Actuator	Active Strain (%)	Active Stress (MPa)	Work Density (kJ/m^3)	Peak Strain Rate (%/s)	Efficiency (%)	Actuation Potential (V)
Mammalian Skeletal Muscle	**20**	**0.35**	**8**	**> 50**	**~ 40**	
Dielectric Elastomers	**Up to 380**	**~ 1**	**Up to 3400**	**4,500**	**Typically 30 up to 90**	**> 1000**
Polypyrrole (conducting polymer)	**2-10**	**Up to 30**	**100**	**12**	**20**	**< 2**
Carbon Nanotube Actuators	**< 1**	**Up to 30**	**2**	**20**	**0.1**	**1**
Liquid Crystal Elastomers (electrically activated)	**2-4**	**0.5**	**~ 20**	**1000**	**75**	**0.1 (for 75 nm thick film)**

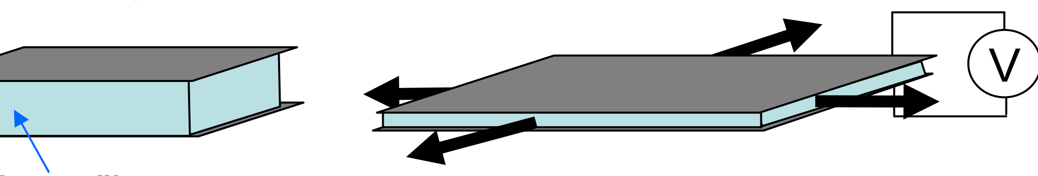
Find more and compare them at http://www.actuatorweb.org

Figure by MIT OCW.

Madden, J. et al. *IEEE Journal of Oceanic Engineering*, 2006 **29**(3) 706

Hunter, I. and Lafontaine, S. *Technical Digest IEEE Solid State Sensors and Actuators Workshop*, 1992, 178-185

Dielectric Elastomers



Dielectric elastomers actuate via application of a strong field across a compliant polymer film

Typical polymers include silicones and acrylic

The pressure (P_z) from attraction between plates is:

$$P_z = \varepsilon_r \varepsilon_o E^2 = \varepsilon_r \varepsilon_o (V/t)^2$$

ε_r = dielectric constant
ε_o = free space permittivity
E = applied electric field
V = applied voltage
t = polymer thickness

Assuming incompressibility, total strain (S) is limited

$$(1+S_x)(1+S_y)(1+S_z) = 1$$

Image of actuator removed due to copyright restrictions.

Advantages: very high strains, strain rates
Disadvantages: requires fields of 150 MV/m or more!

(SRI International)

Polypyrrole Actuation

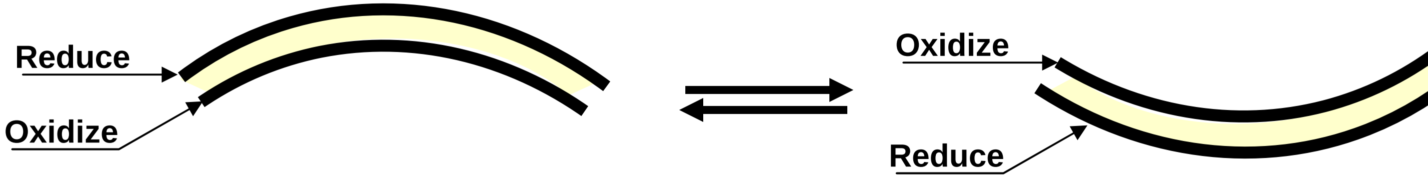
Polypyrrole actuates via redox-driven ion incorporation and expulsion

This is typically measured in a wet electrochemical cell, but encapsulated trilayers can also be produced for actuation in air

Linear Actuation

Schematic of linear actuation and trilayer structure removed due to copyright restrictions.

Trilayer Actuation



Advantages: low power, decent actuation metrics, room for improvement
Disadvantages: slow