Organic Metals and related materials - synthesis and physical properties.

Conductivity

$$\vec{j} = \sigma \vec{E}$$

- σ − conductivity (przewodność właściwa)
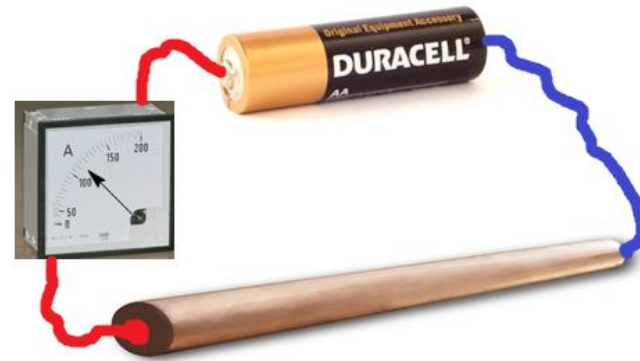- $\vec{j}$ − electric curent density
- $\vec{E}$ − electric field intensity

$$\sigma = \frac{l * G}{S}$$

- G – electrical conductance (przewodnictwo elektryczne) [S] Siemens
- l – lengh [m]
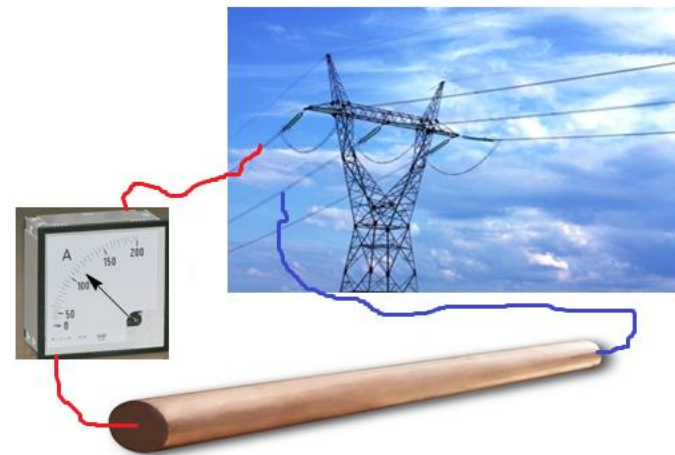- S – cross-section area [m^2]

$$\sigma = \left[\frac{1}{\Omega * m}\right] = \left[\frac{S}{m}\right]$$

- R – electrical resistance [Ω] Ohm

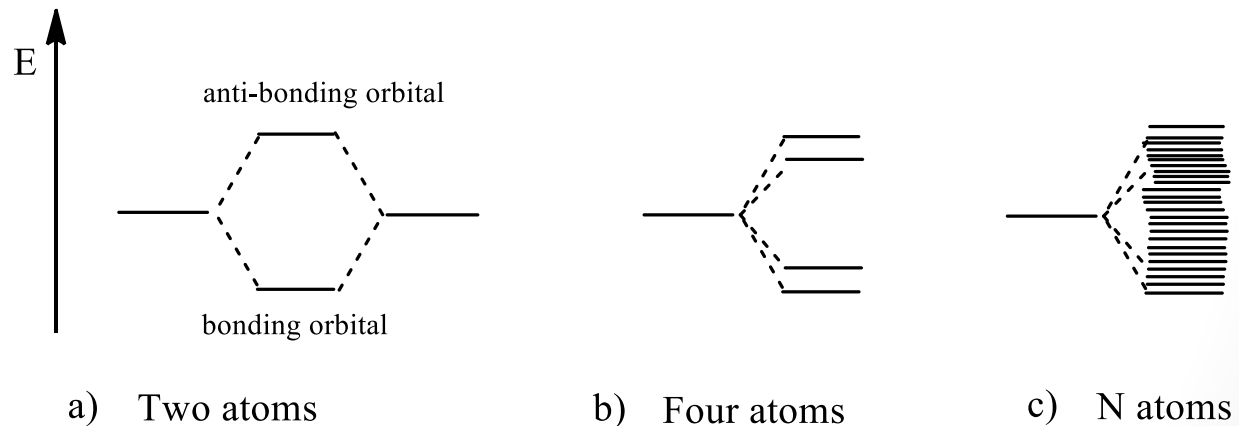$$R = \frac{1}{G} = \left[\frac{1}{S}\right]$$

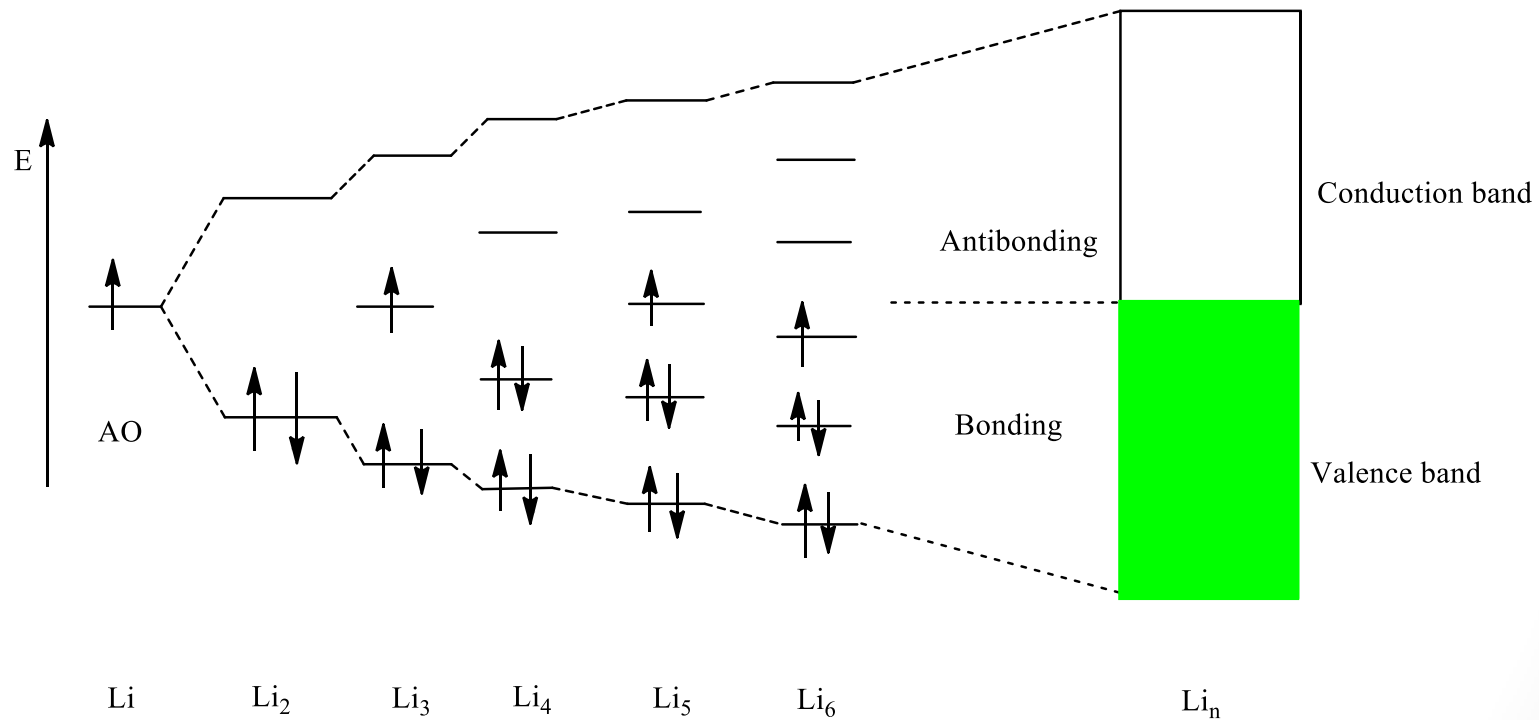High conductivity

Low conductivity

2

Conductivity

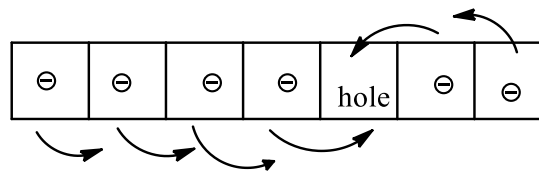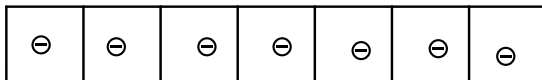| Material	Conductivity [S/m]	
Silver	6.30×10^7	**Conductors** 10^3 - 10^8
Copper	5.96×10^7	
Gold	4.10×10^7	
Steel	6.99×10^6	
Carbon Graphite	$3.30 \times 10^2 \perp$ up to $3.00 \times 10^5 \parallel$	
Germanium	2.17	**Semiconductors** 10^{-8} - 10^3
Silicon	1.56×10^{-3}	
Sea Water	4.80	
Wood (dry)	10^{-14}	**Insulators** 10^{-25} - 10^{-8}
PCV	10^{-16}	
Poliethylene	10^{-22}	
Teflon	10^{-25} to 10^{-23}	

Band Theory of Solids

- Does metalic Lithium conduct electricity?
- Why metalic Lithium conduct electricity?

- Li $1s^2\ 2s^1$

E

anti-bonding orbital

bonding orbital

a) Two atoms   b) Four atoms   c) N atoms

4

Band Theory of Solids

E

AO

Antibonding

Bonding

Conduction band

Valence band

Li   Li$_2$ Li$_3$ Li$_4$ Li$_5$ Li$_6$ Li$_n$

Band Theory of Solids

E

Conduction band

Valence band

$\Delta E < 3eV$

$\Delta E > 3eV$

Metal
(conductror)
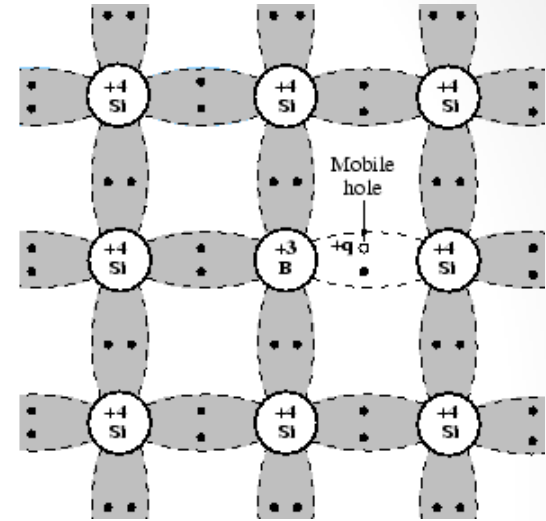
Semiconductor
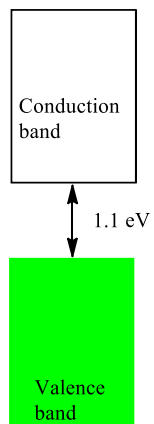
Si, Ge, GaAs, PbS,
InAs

Insulator

PVC, PE, glass

hole
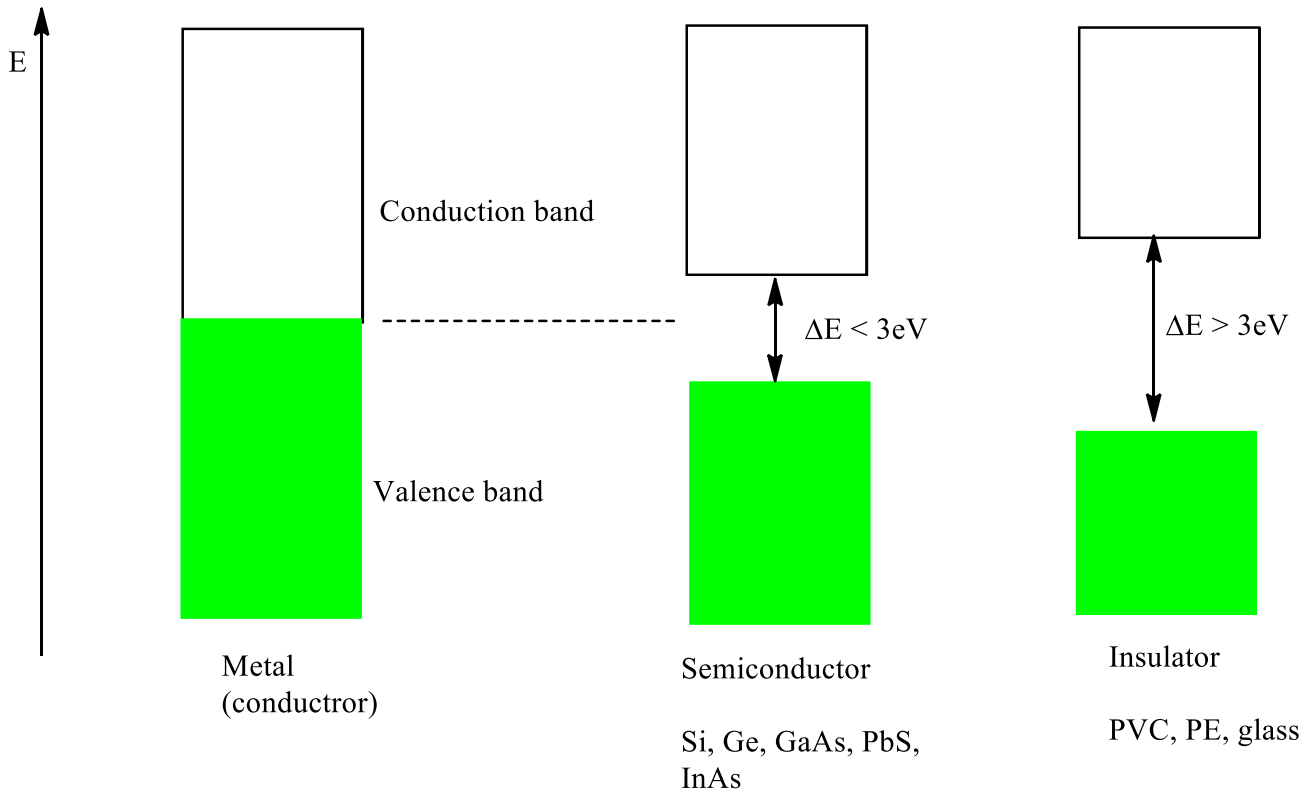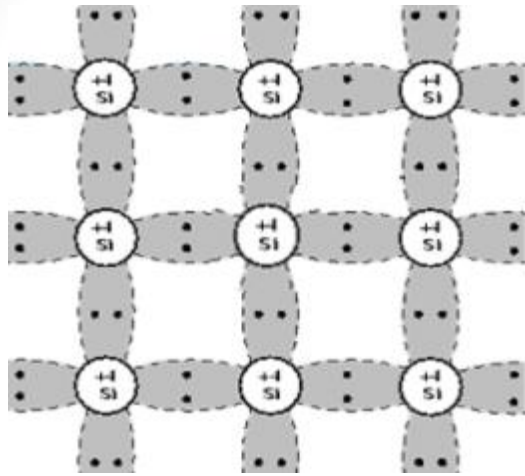
Semiconductors

Silicon without impurities

n-type

p-type

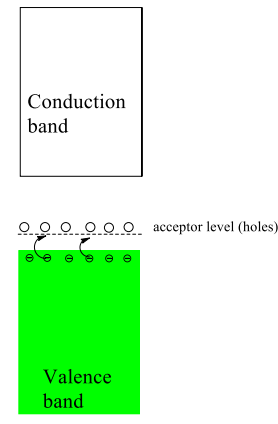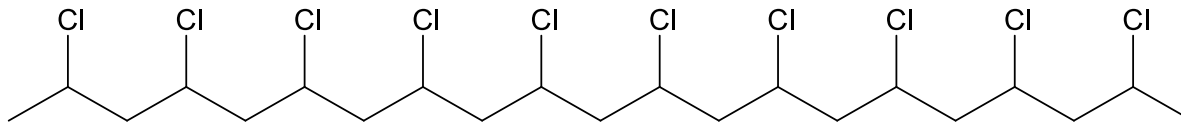Conduction band

1.1 eV

Valence band

Semiconductor

Conduction band

Donor level (extra electrons)

Valence band

n-type Semiconductor

Conduction band

acceptor level (holes)

Valence band
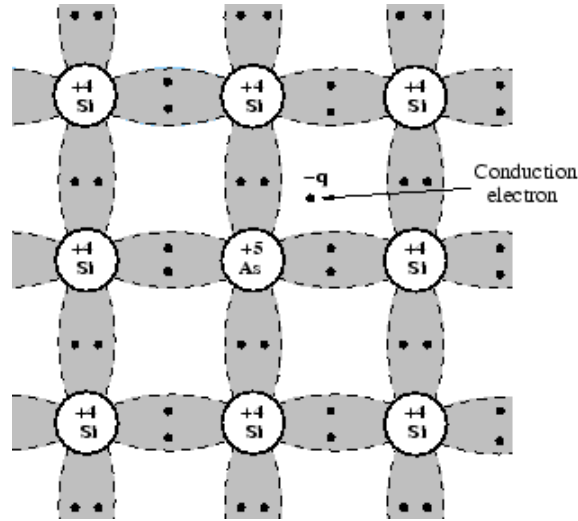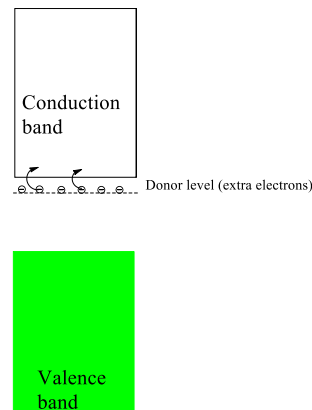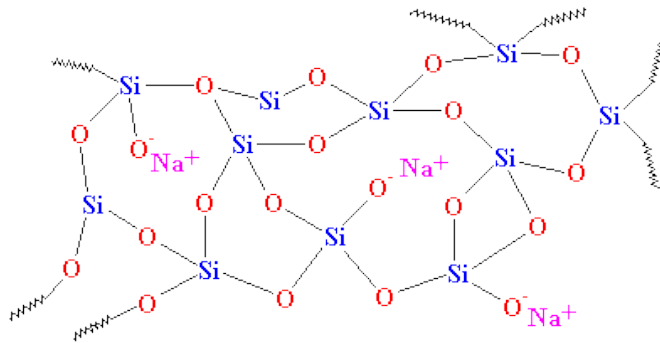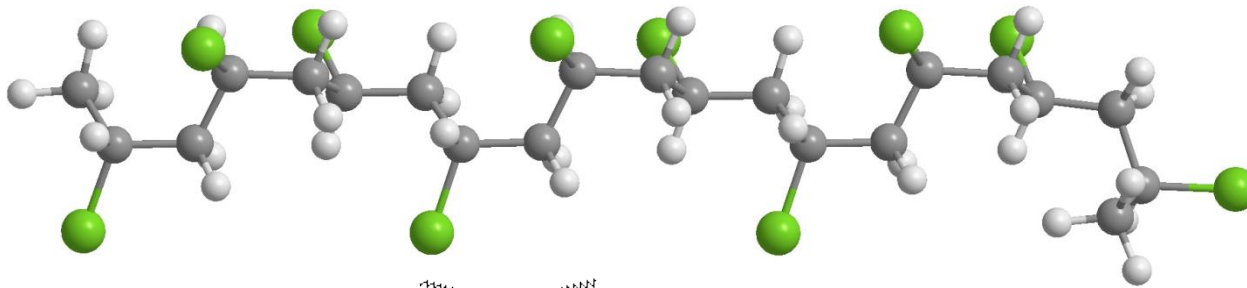
p-type Semiconductor
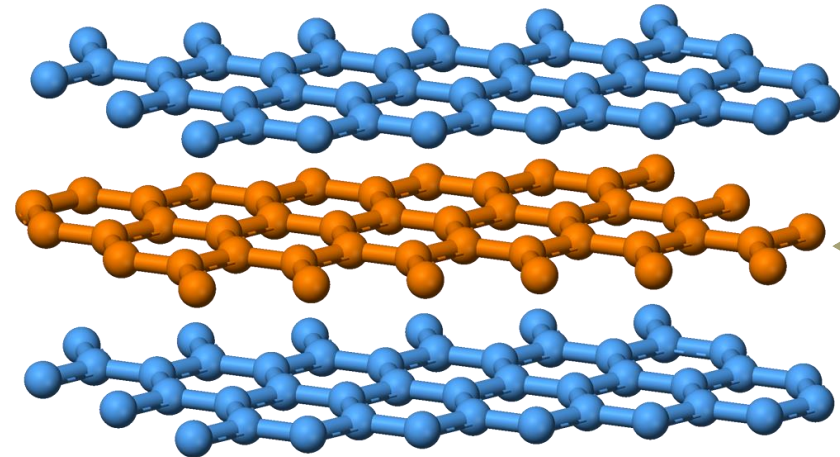
Insulators

PVC ΔE = 6 eV

Light's photons energy
500 nm 2.5 eV (green)
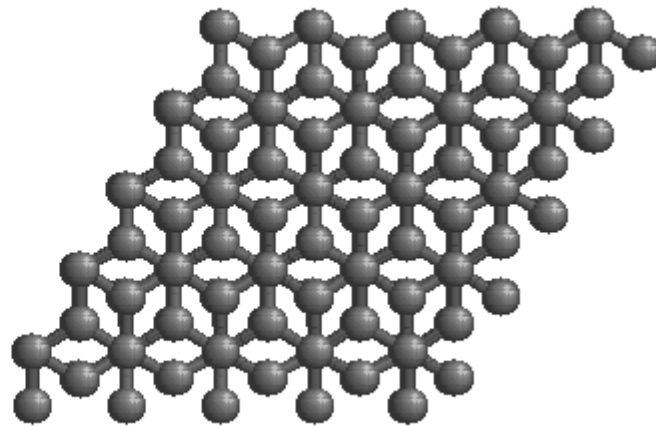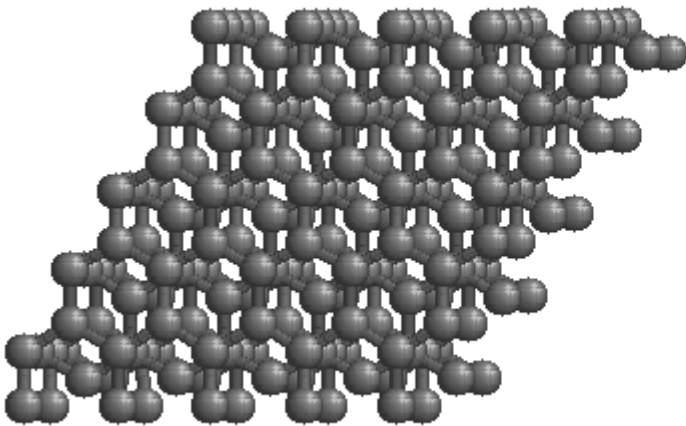400 nm 3.1 eV
288 nm 4.3 eV

Lots of insulators are transparent for light.
The visible light photons do not have enough energy to
bridge the band gap and get the electrons up to an available energy level
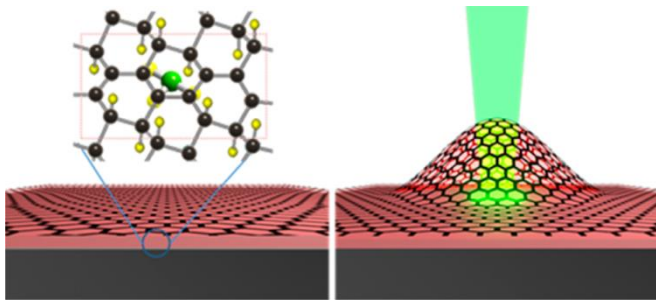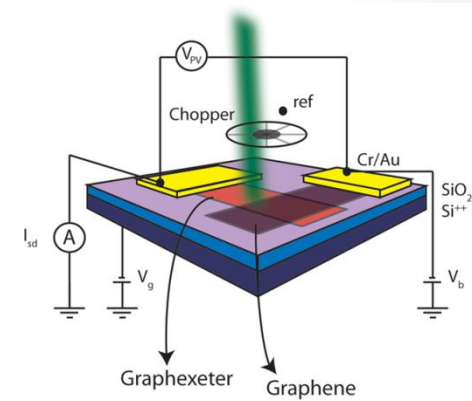in the conduction band.

Graphite

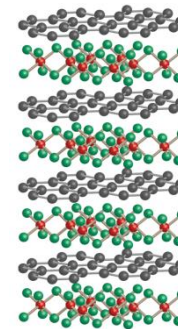Better conductivity
3.00×10^5 [S/m]

Graphene

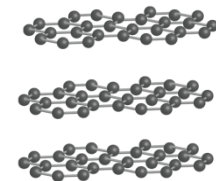**Nanometer Thick Elastic Graphene Engine**

Graphene treated with ClCF$_3$, 532 nm Laseer as ignition plug, 10000 cycles.
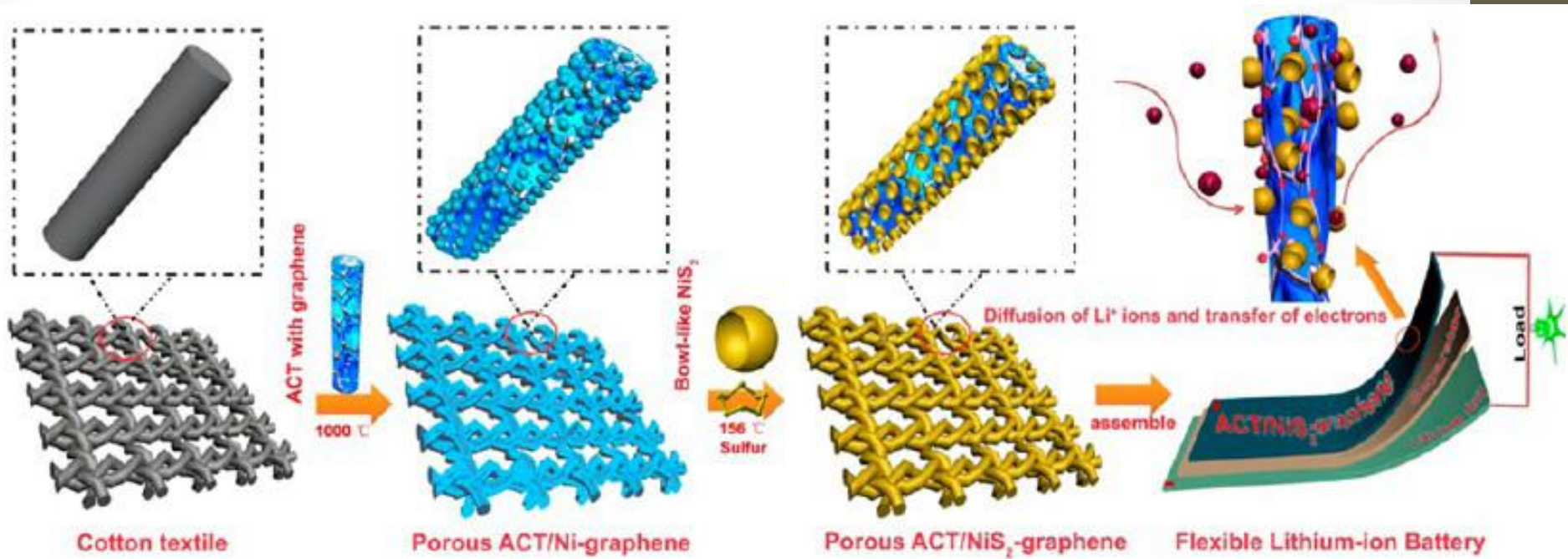*Nano Lett.*, **2014**, *14* (5), pp 2677–2680

FeCl$_3$ - FLG

FLG

Graphene Photodetectors

Nano, **2013**, *7* (6), pp 5052–5057

10

Graphene

Cotton textile → Porous ACT/Ni-graphene → Porous ACT/NiS₂-graphene → Flexible Lithium-ion Battery

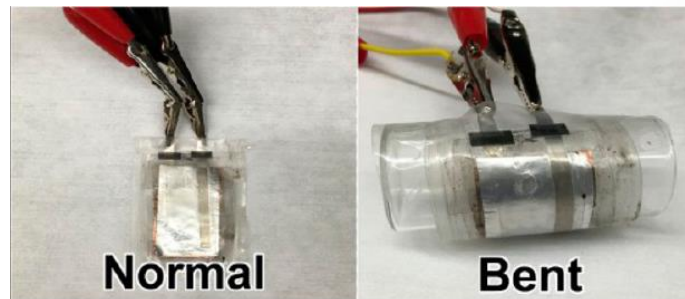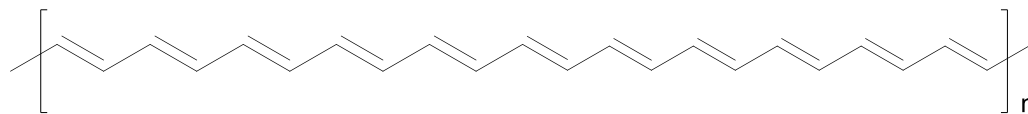**Cotton-Textile-Enabled, Flexible Lithium-Ion Batteries with Enhanced Capacity and Extended Lifespan**

Discharge capacity ~1710 mAh g−1 at 0.01 C), and the discharge capacitance retained at ~645 mAh g−1 at 1 C after 100 cycles
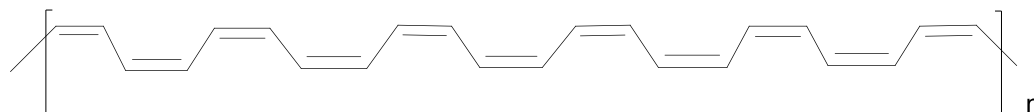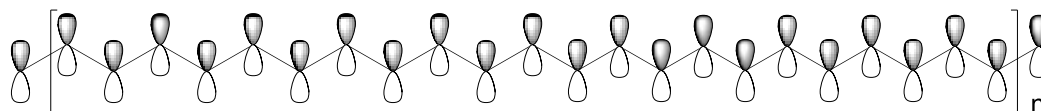

Normal   Bent

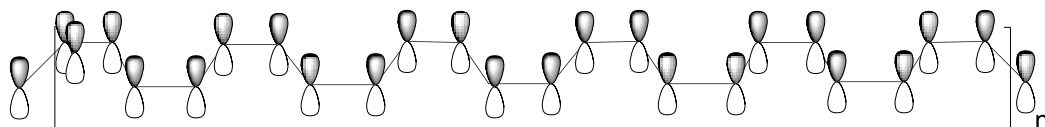*Nano Lett.*, **2015**, *15* (12), pp 8194–8203

11

Conducting polymers

trans- polyacetylene

cis- polyacetylene

First studies on acetylene polymerization were reported in 1866 by Berthelot. The first extensive investigations into the polymerization of acetylene, using Ziegler-Natta catalysts, were performed by Natta and coworkers in 1958.

Poly-acetylene

100°C

Ti(OPr)$_4$ / Al(Et)$_3$

H——≡——H

Silvery film, semiconductor with ΔE = 1.7 eV

conductivity: trans 10^{-3} S/m;   cis 10^{-7} S/m

150°C

-80°C

WCl$_6$ / Ph$_4$Sn

110°C
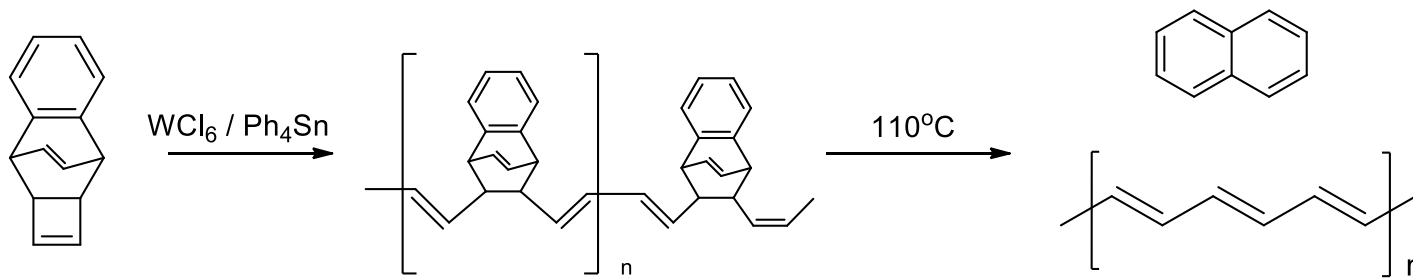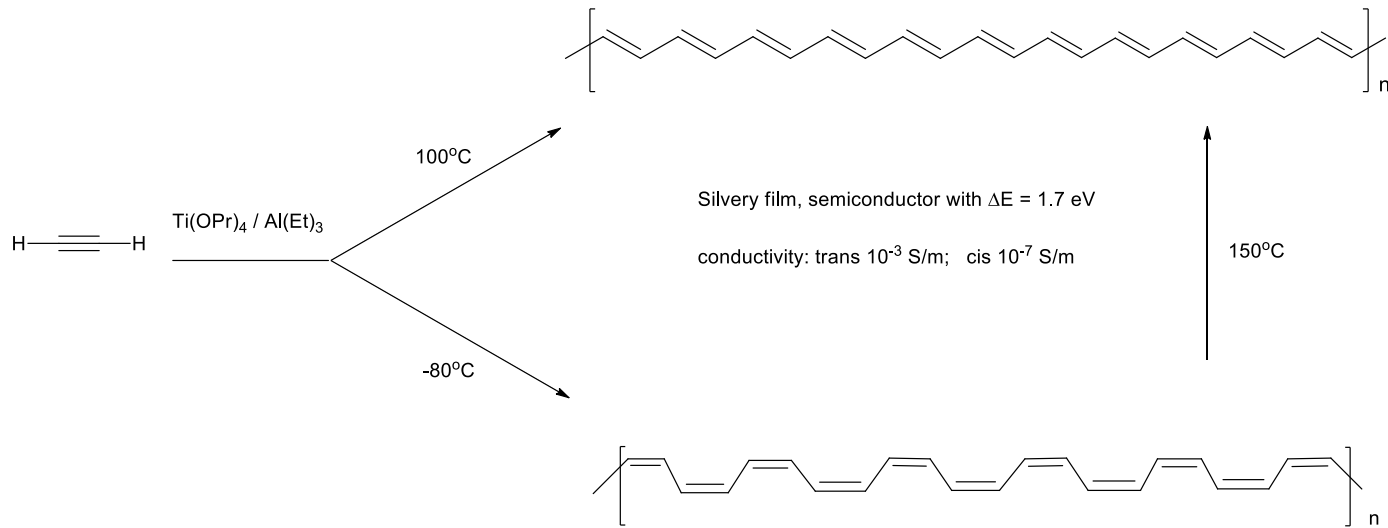
ROMP
Methathesis polymerization

European Pat. Appl. No. 82306139.5

13

Peierls transition

metalic state

full electron delocalization

n

Peierls Transition

semiconcuctor state

conjugated double bond

n

E

Conduction band

Peierls

transition

$\Delta E = 1.7$ eV

Valence band

10000K

metal

"ideal" Polyacetylene

semiconductor

"real" Polyacetylene

134.06pm

butadiene

145.74 pm
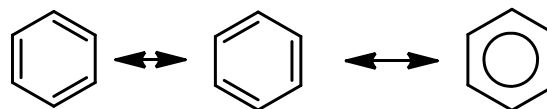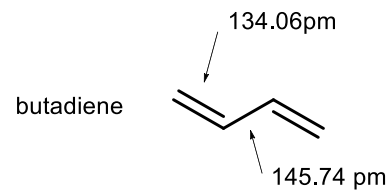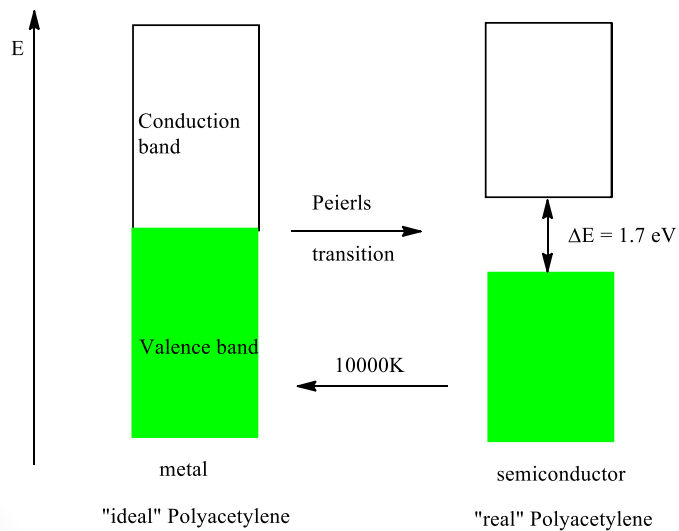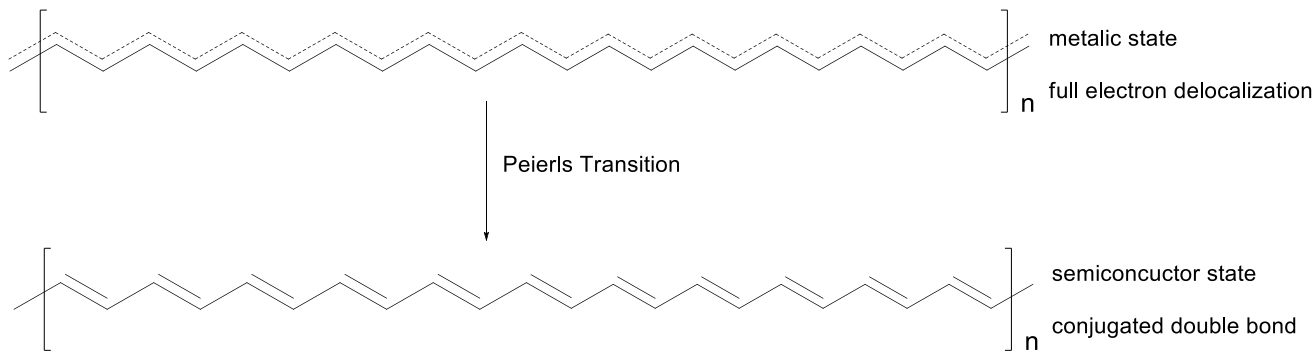
"metallic behavior"

Doping of Polyacetylene

SET

I$_2$

positive polaron

translation of charge

I$_2$

positive bisoliton
(bipolaron)

[PA] + 3I$_2$ ⟶ [PA]$^{++}$ + 2I$_3^-$

SET

K

negative polaron

[PA] + K ⟶ [PA]$^-$ + K$^+$

E

$\Delta E = 1.7$ eV

doping

CB

bipolaron bands

VB

positive bipolaron

15

Doping of Polyacetylene

positive bisoliton (bipolaron)

positive polaron

negative polaron

$H_2C{=}CH_2$ p — π^* — p π

$H_2C{=}C{-}CH_2$ $\overset{\oplus}{}$ π^* — NBMO π
        H

$H_2C{=}C{-}CH_2$ $\bullet$ π^* NBMO π
        H

$H_2C{=}C{-}CH_3$ π^* NBMO π
        H

16
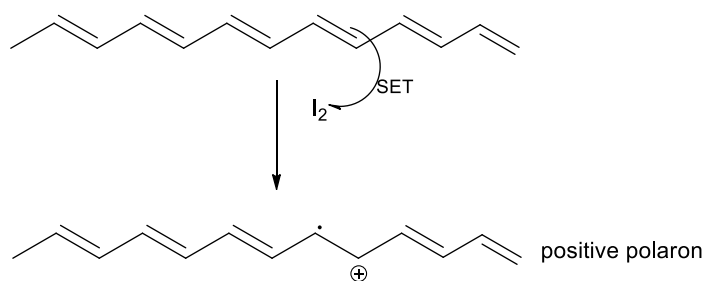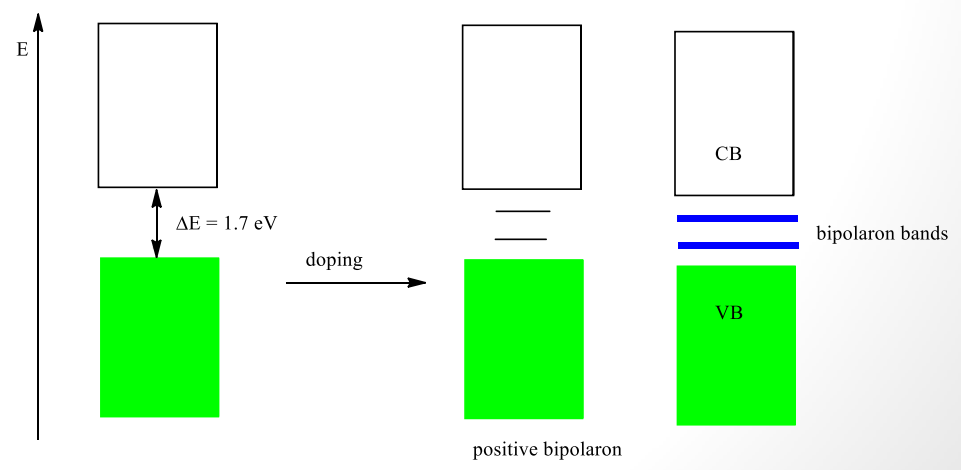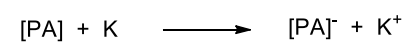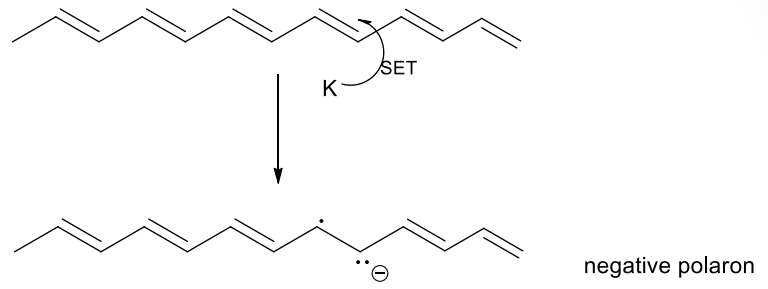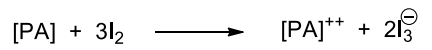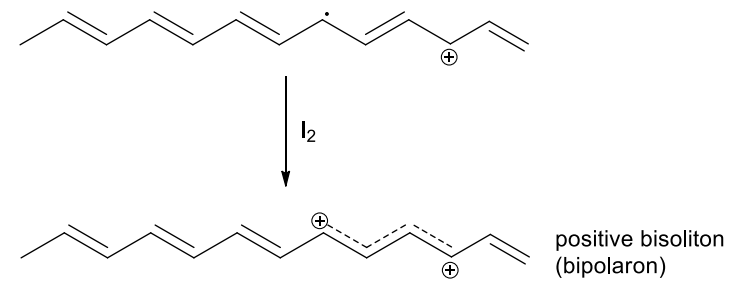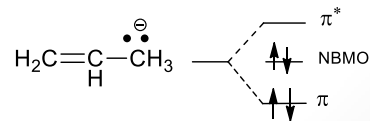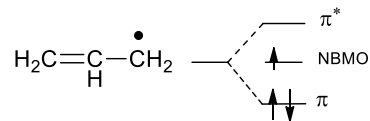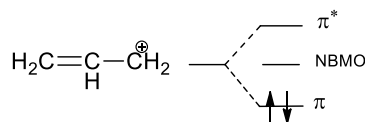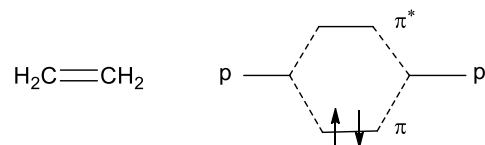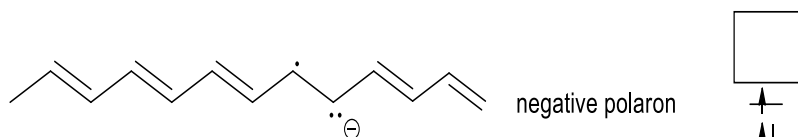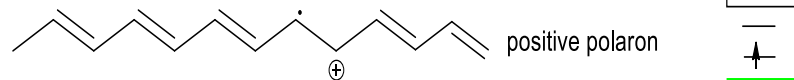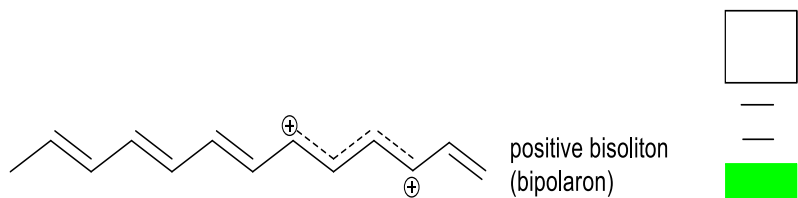
Conducting polymers

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"* polyacetylene can be made conductive almost like a metal !

Alan G. MacDiarmid
Professor at the University of Pennsylvania,
Philadelphia. USA.

Hideki Shirakawa
Professor Emeritus,
University of Tsukuba. Japan.

Alan J. Heeger
Professor at the University of California
at Santa Barbara. USA.

In 1977 Shirakawa prepared poliacetylene with conductivity as high as 56 000 S/m by doping it with chlorine, bromine, iodine, and arsenic pentafluoride.

vacuum state	undisturbed conjugation
neutral soliton	free radical
positive soliton	carbocation (carbenium ion)
negative soliton	carbanion
positive polaron	radical cation
negative polaron	radical anion
positive bisoliton (bipolaron)	carbodication
negative bisoliton (bipolaron)	carbodianion
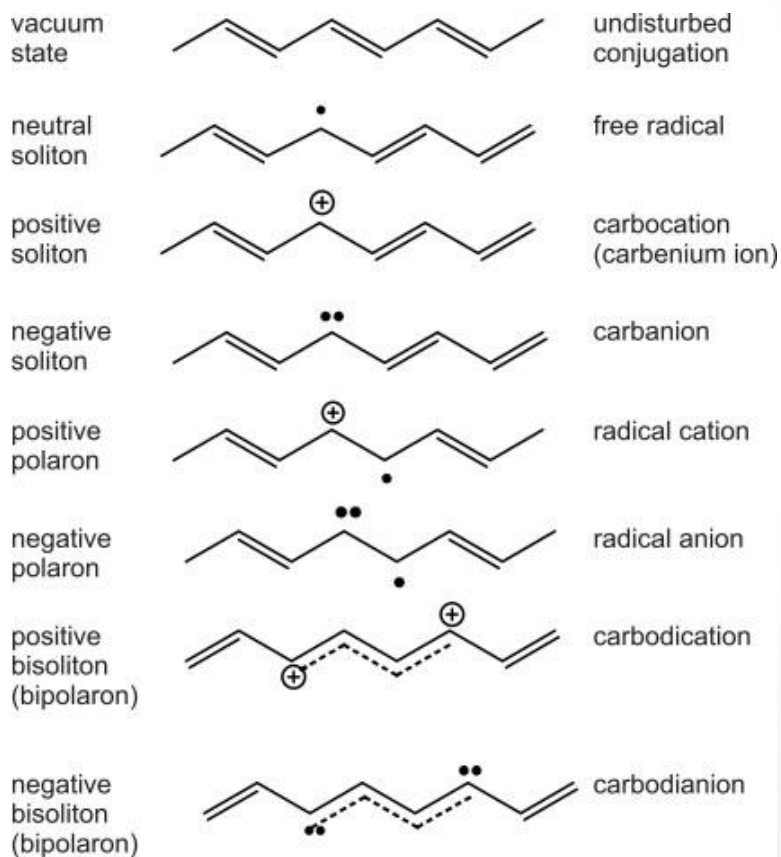
Poly-acetylene coplanarity problems
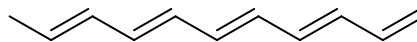
doped with I_2

> 10 S/cm
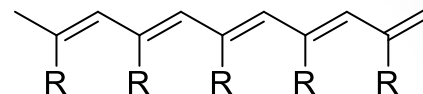
R = Me, Br, Cl
doped with I_2;   < 0.001 S/cm
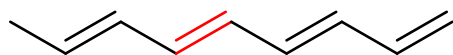
full overlaping

- Coplanarity gives best overlaping between π orbitals
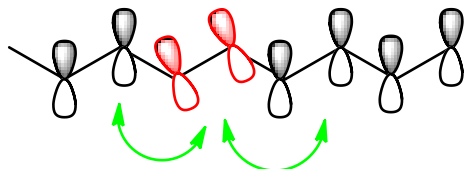
partial overlaping

- Distortion from coplanarity reduces the electron mobility
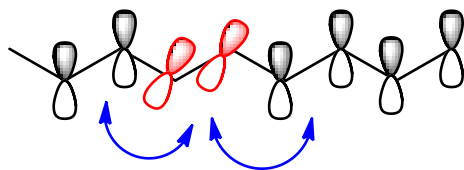
no overlaping

- 90° distortion lead to conjugation defects

Polyaniline
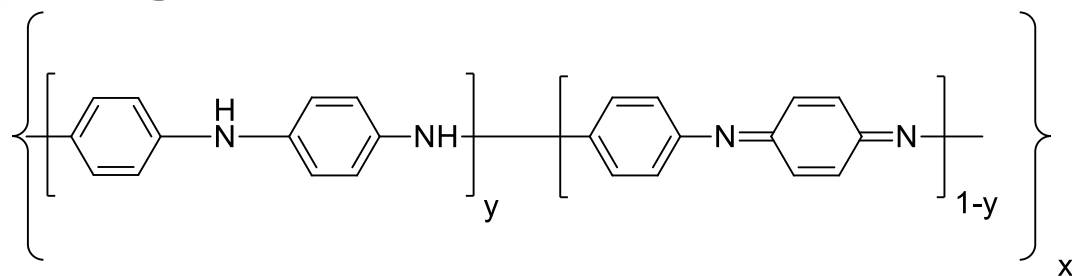
leucoemeraldine – white, clear y =1 - fully reduced
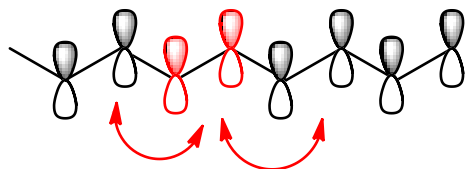**pernigraniline** – blue y =0 - fully oxidized
emeraldine – green for the emeraldine salt, blue for the emeraldine base y =1/2
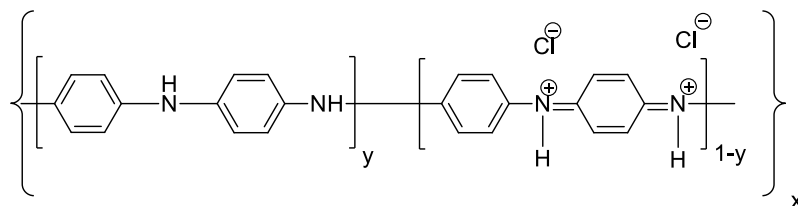
Conductivity 500 S/m

leucoemeraldine – also can be oxidized with $FeCl_3$, $SnCl_4$, NO_2
Conductivity up 100 S/m

Polyaniline - preparation
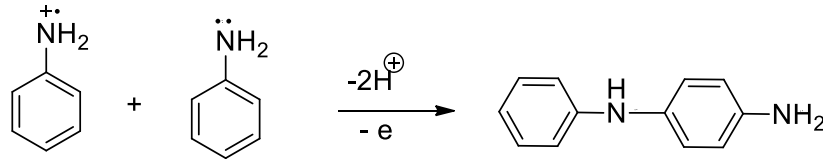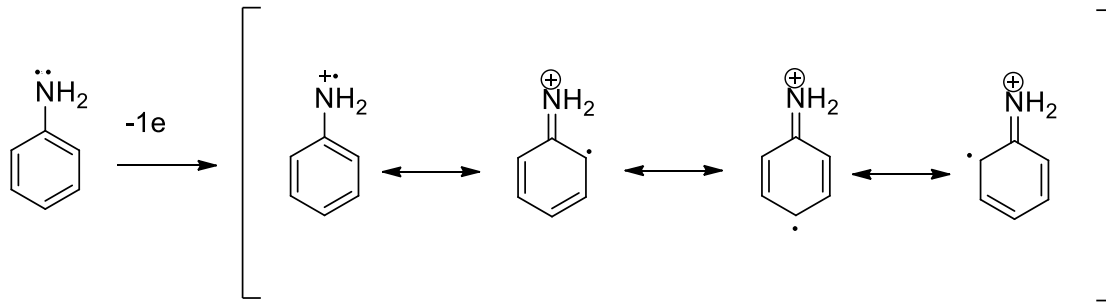
oxidizers: $(NH_4)_2S_2O_8$, $Ce(SO_4)_2$, UHP urea*H_2O_2

Polypyrrole

Anodic oxidation
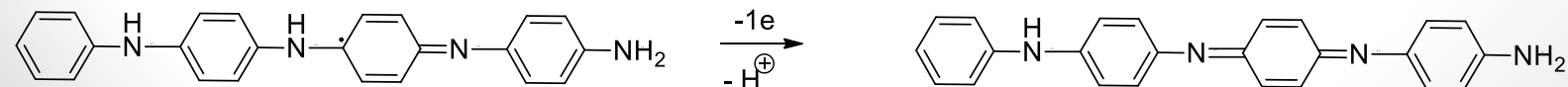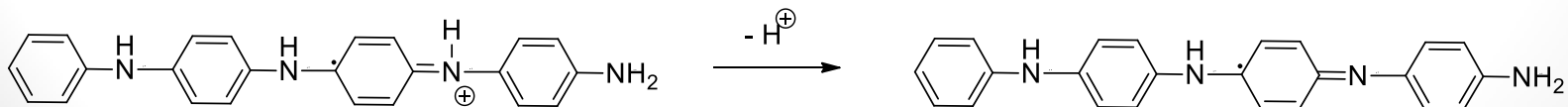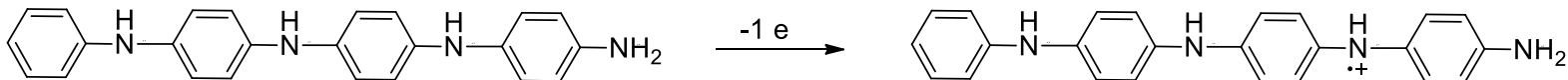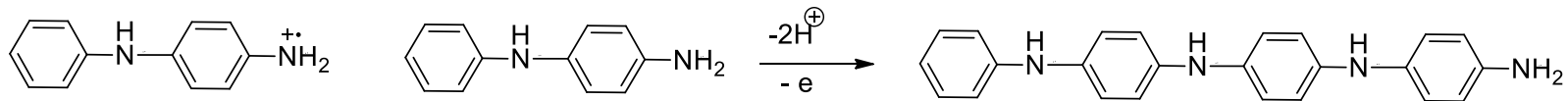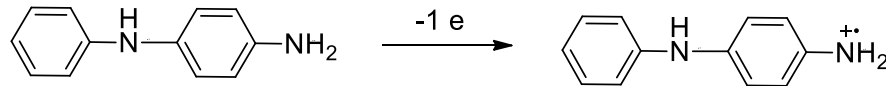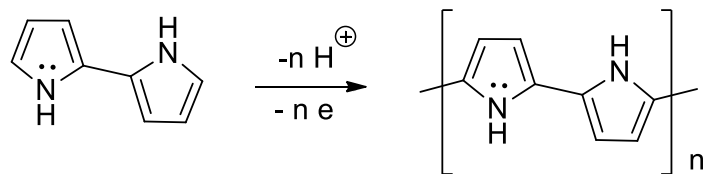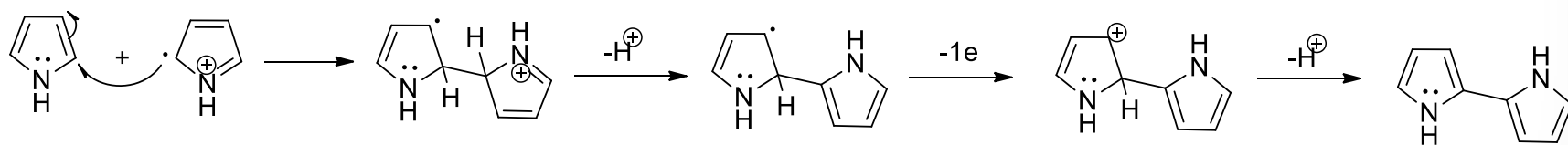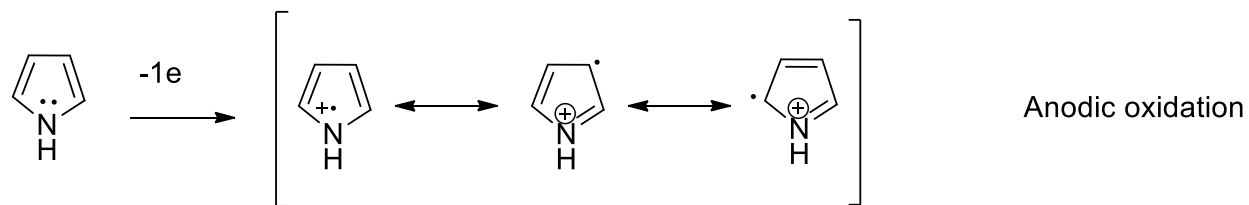
Polypyrrole
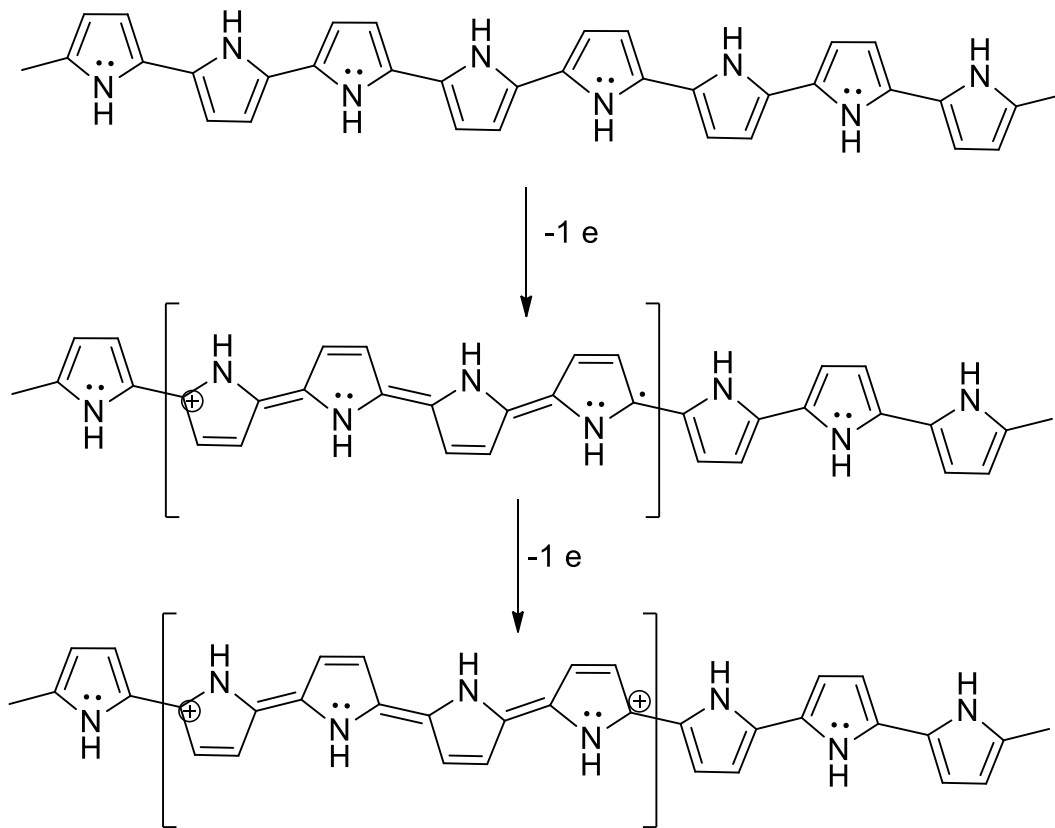
750 000 S/m

Polyphenylenes
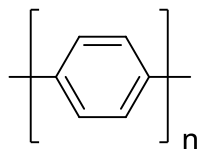
poly(p-phenylene)
PPP
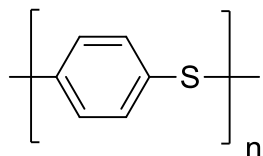
poly(phenylenesulfide)
PPS
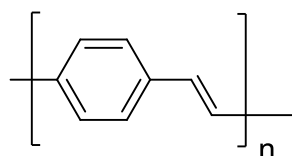
poly(phenylene vinylene)
PPV
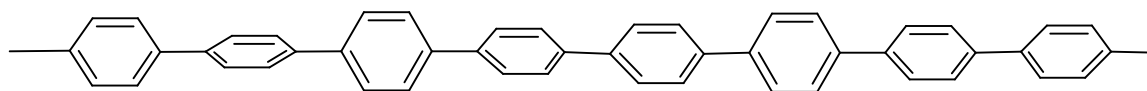
ΔE 0.2 - 3 eV
depends on rotation angle

THF / H$_2$O

NaHCO$_3$
Pd(PPh$_3$)$_4$
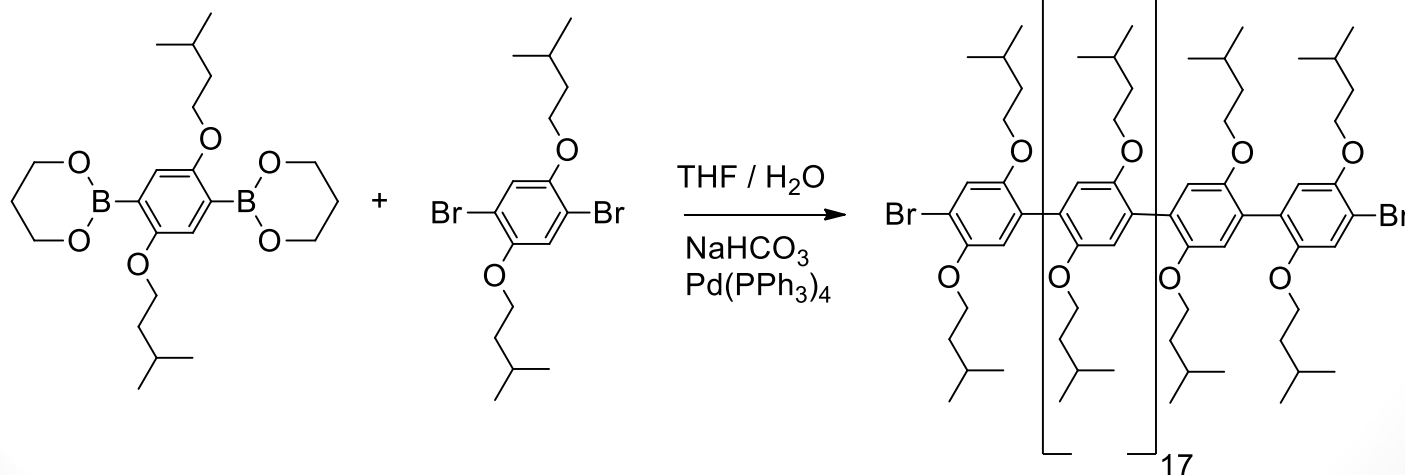
Synthesis of low molecular weight poly(*p*-phenylene)s (PPP)

23
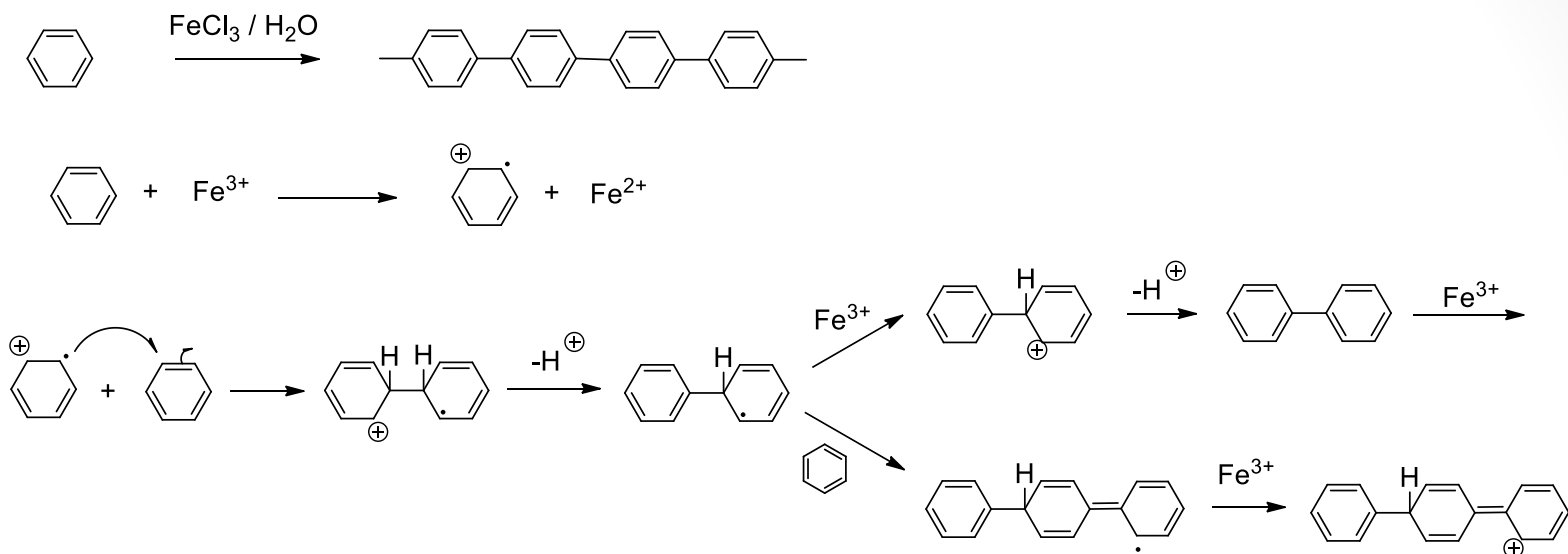
Polyphenylenes

p-Polyphenyl from Benzene-Ferric Chloride.
Water **(1** mole) was added dropwise with stirring
under nitrogen at **10-25'** to a mixture of benzene (2 moles) and
ferric chloride **(1** mole). The reaction mixture was heated during
20 min. to **70** i **3';** whereupon hydrogen chloride was rapidly
evolved and the contents darkened. After **30** sec., the mixture
was quickly cooled and filtered. The residue was washed with
benzene and then triturated repeatedly with boiling concentrated
hydrochloric acid until the filtrate was colorless. After the
polymer was treated with hot **2** *M* sodium hydroxide, the acid
triturations were repeated. The red-brown solid was washed
thoroughly with distilled water, and dried at **14C-150°** for **2** hr.

24

Poly(phenylenesulfide)

$$Cl-\langle\bigcirc\rangle-Cl + Na_2S \xrightarrow{260^oC} S-\langle\bigcirc\rangle-S-\langle\bigcirc\rangle-S-\langle\bigcirc\rangle-S-\langle\bigcirc\rangle-S$$
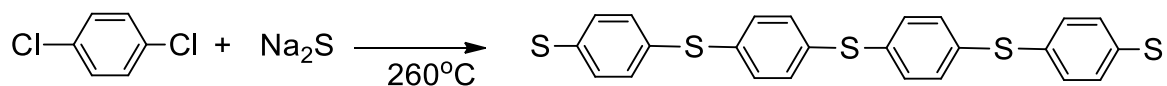
Insulator
Must be oxidized or doped

Tedur, DURAFIDE

Very high thermal resistance (above> 260 ° C)
• Very high operating temperature (up to 240 ° C)
• Very high rigidity and hardness
• excellent hydrolysis resistance

EP 0240016 A2A
Stainless steel autoclave equipped with a partial condenser
and having a capacity of I liter was charged with 91 g (0.7 mole)
of flaky sodium sulfide hydrate (Na_2S content = 60%) and 315 g
of N- methylpyrrolidone, and dehydration was carried out under
heating by circulating nitrogen gas. When the amount of aqueous
N-methylpyrrolidone distilled at a temperature of 2I0°C reached
148 g, the mixture was cooled to 170 °C. Then, 102.9 g (0.7 mole)
 of p-dichlorobenzene was added to the reaction mixture and reaction
was carried out under a nitrogen gas pressure of 2 x I05 Pa
under stirring for 2 hours at 220 °C and or 3 hours at 260°C.

Characteristics of SO₃-Doped PPS

SO_3 press., torr	time exposed to SO_3, min	time open to vacuum, min	max conduct.		steady-state conduct.	
			S/cm	time	S/cm	time, days
26	1220	155	1.7×10^{-5}	40 min	1.4×10^{-5}	2
40	40	a	2.4×10^{-4}	3.2 days	1.8×10^{-4}	4.1
60	45	a	1.4×10^{-4}	155 min	2.4×10^{-5}	6.8
112	265	b	2.0×10^{-4}	35 min	6.3×10^{-5}	8.8
260	60	90	1.6×10^{-4}	85 min	1×10^{-4}	6

^{a} Kept under dynamic vacuum to end of experiment. ^{b} Nitrogen added and not evacuated.

$$SO_3 + 2e \longrightarrow SO_3^{2-}$$

$$2SO_3 + 2e \longrightarrow SO_3^{2-} + SO_2$$

25
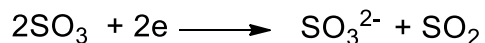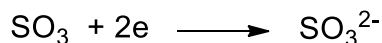
Macromolecules **1985,18, 2389-2394**

Poly(phenylevinylene)
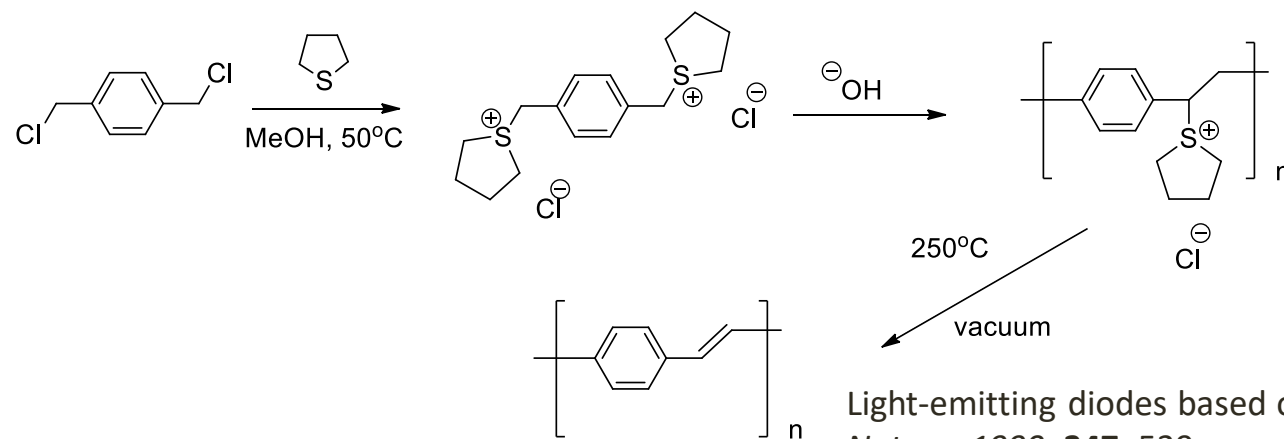
Light-emitting diodes based on conjugated polymers
Nature, *1990*, **347**, 539

26
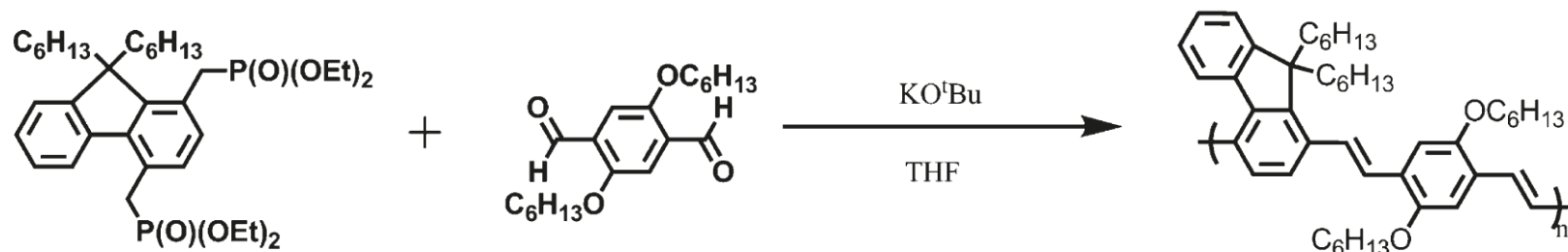
Gilsh polymerization
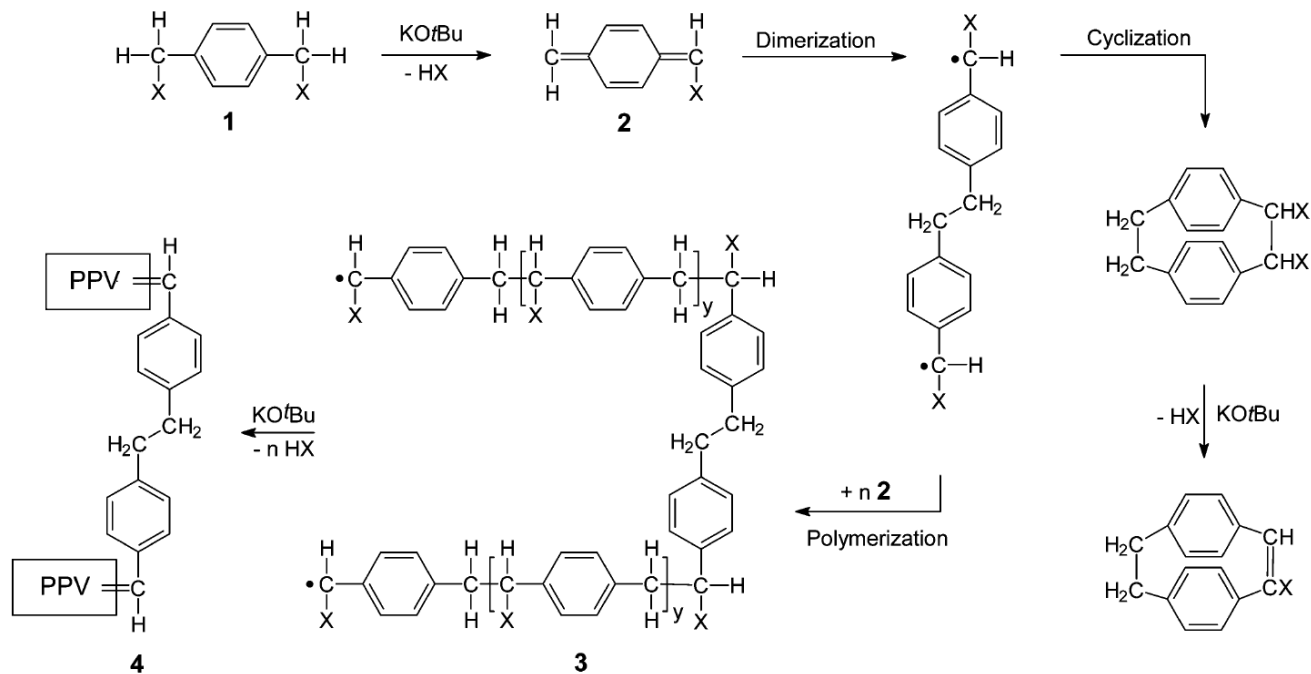
Macromolecules **2007,** *40,* 8842-8854

TEMPO

Poly(phenylevinylene)

- Abs. (in THF)
- PL @ excitation 400 nm
- EL @ 15 V
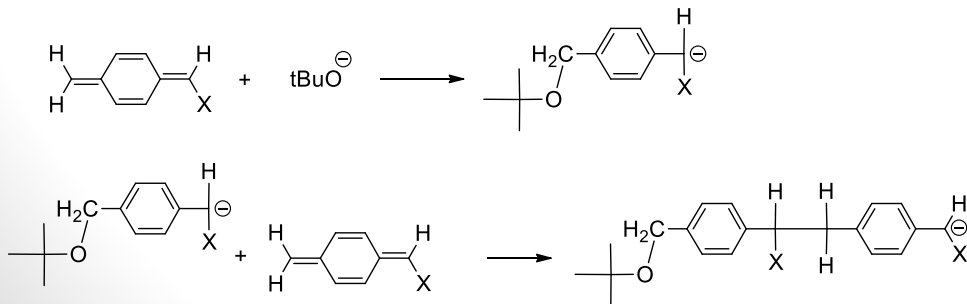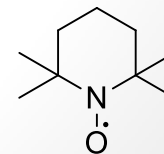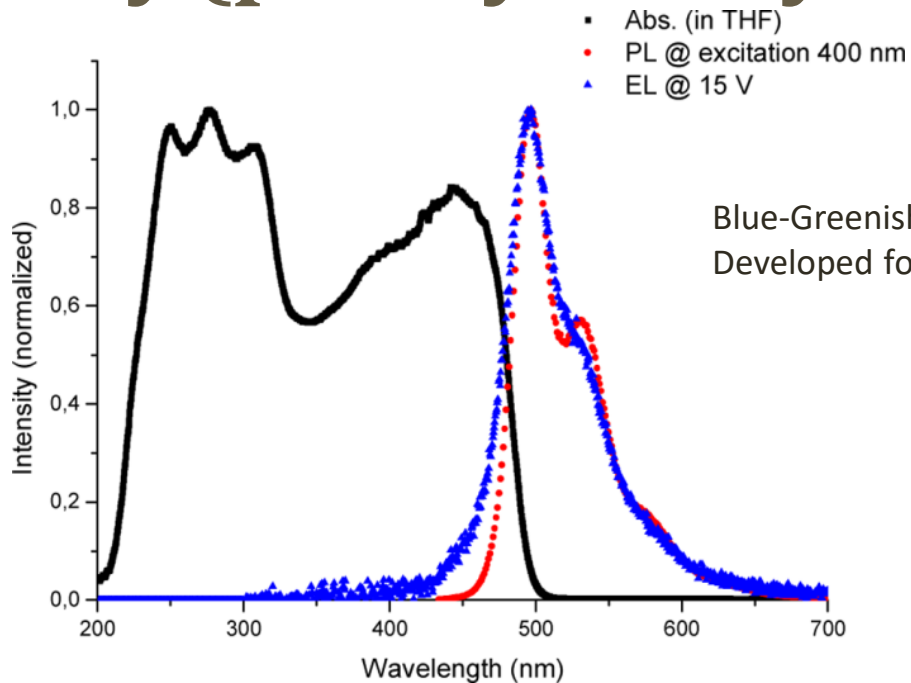
Blue-Greenish Electroluminescent Poly(p-phenylenevinylene) Developed for Organic Light-Emitting Diode Applications

Ultraviolet−visible (UV−vis), photoluminescence (PL), and electroluminescence (EL) spectra of the C48C48 PPV.

Macromolecules **2016**, *49*, 1674−1680

Poly(3,4-ethylenedioxythiophene) :poly(styrenesulfonate) PEDOT:PSS

ITO indium tin oxide

Ca, Al
OC$_{48}$C$_{48}$ PPV
PEDOT:PSS
ITO
glass substrate

OC$_{48}$C$_{48}$ PPV

28

Poly(phenylevinylene)

CH$_3$O— ... OCH$_3$

BF$_4^-$

CH$_3$CO— ... —OCH$_3$

OCH$_3$

CHO

H$_3$C— ... —CH$_3$
$\xrightarrow{BF_3 \cdot Et_2O}$
H$_3$C— ... —CH$_3$
7
$\xrightarrow[Ac_2O]{CH_3O— —CH_2COONa}$
H$_3$C— ... —CH$_3$
8
$\xrightarrow[H_2O]{HBr}$

HO ... OH

OH

H$_3$C— ... —CH$_3$
9
$\xrightarrow[K_2CO_3]{Br}$
H$_3$C— ... —CH$_3$
10
$\xrightarrow[CCl_4]{NBS}$

BrCH$_2$— ... —CH$_2$Br
11
$\xrightarrow[THF]{t\text{-}BuOK}$
P2
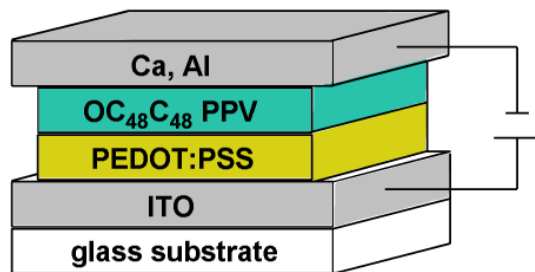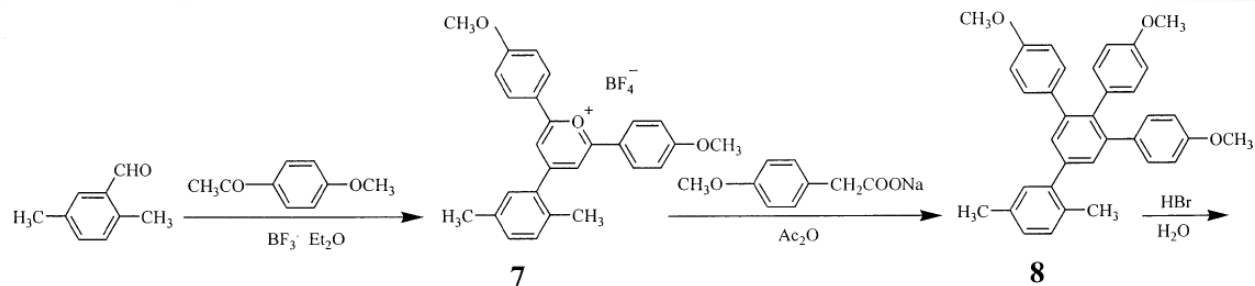
UV−Vis, PLE, and PL Data of Polymers

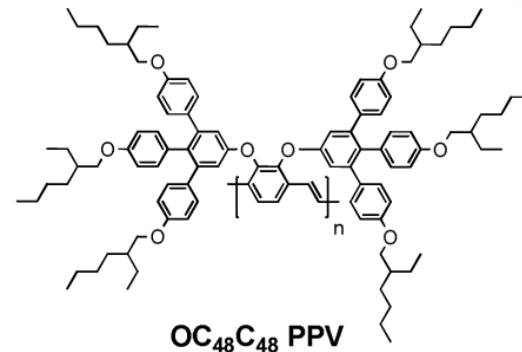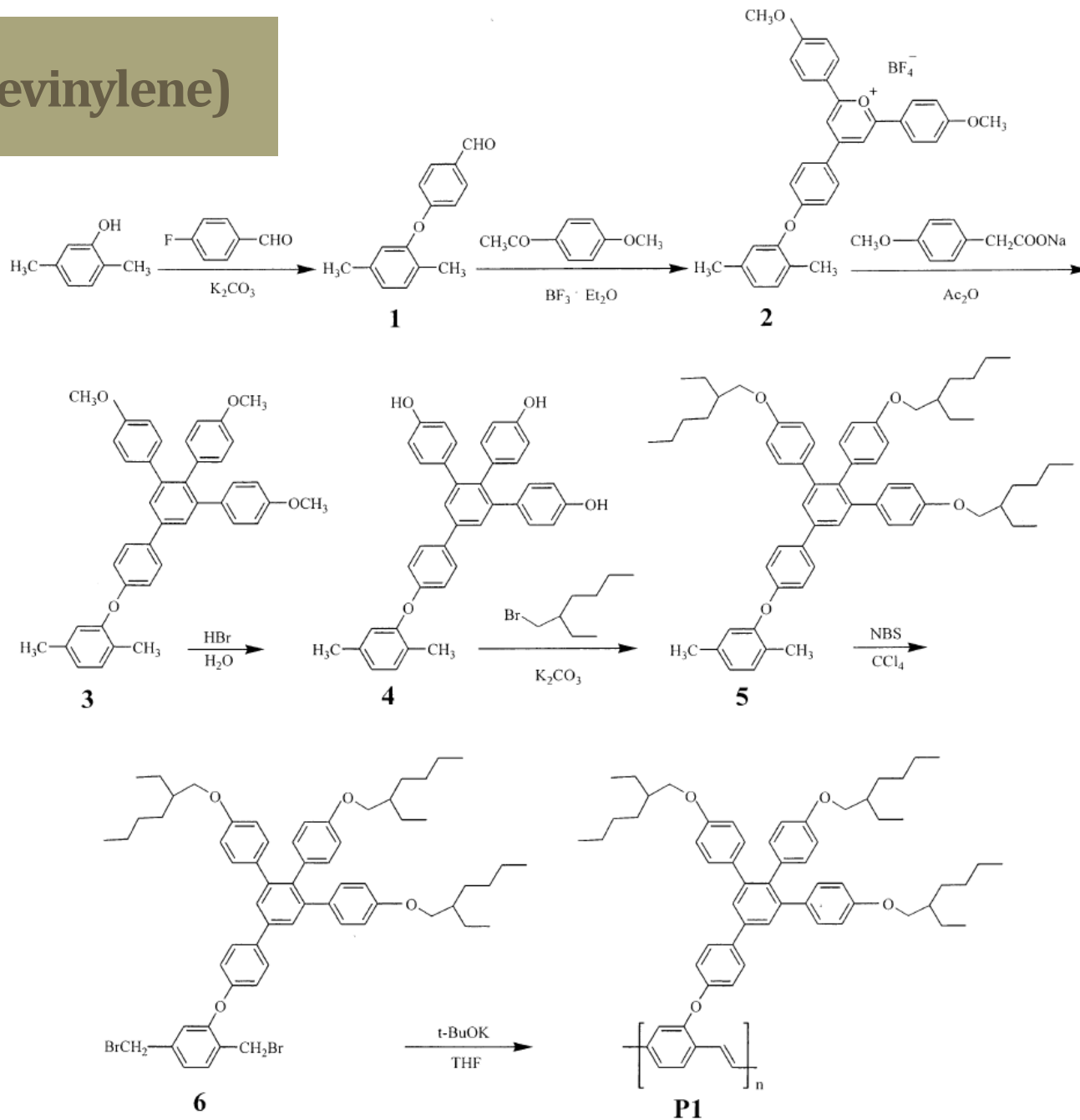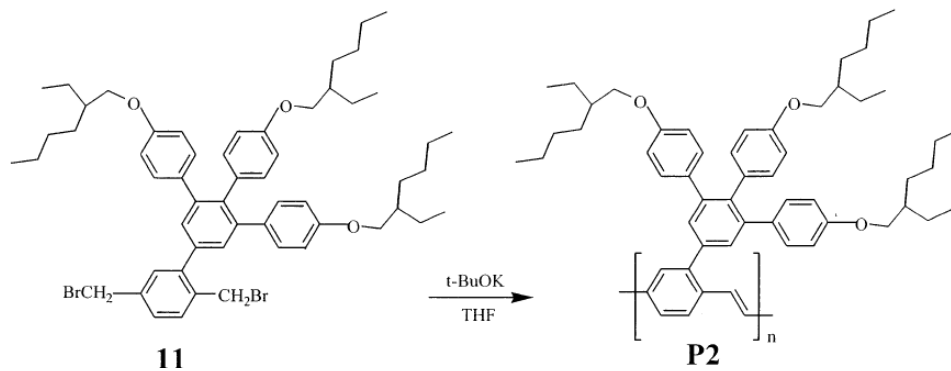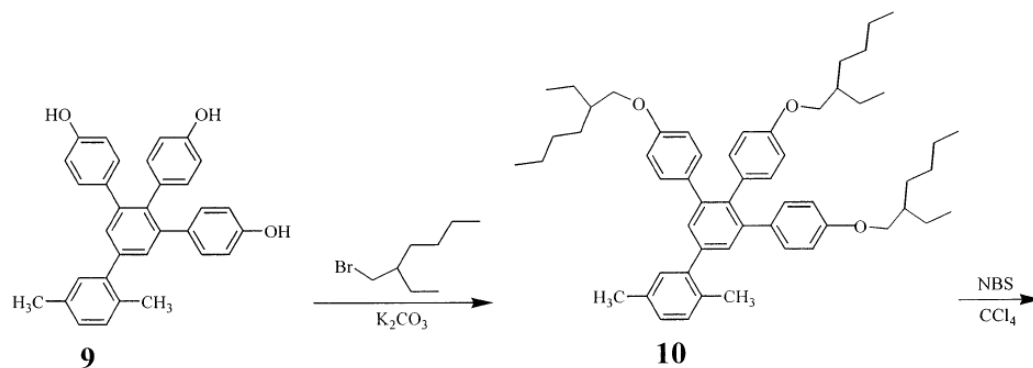| polymer	$\lambda_{a,max}{}^a$ in solution (nm)	$\lambda_{ex,max}{}^b$ in solution (nm)	$\lambda_{f,max}{}^{c,d}$ in solution at RT (nm)	$\lambda_{f,max}{}^{c,d}$ in solution at ca. −50 °C (nm)	$\Phi_f{}^e$ in solution	$\lambda_{ex,max}{}^b$ in thin film (nm)	$\lambda_{f,max}{}^c$ in thin film (nm)
P1	277	390	455	455, 514	0.12	402, 431	476
P2	267	388	428, 452	453	0.10	397, 425	476

^{a} $\lambda_{a,max}$: the absorption maxima from the UV−vis spectra in THF solution. ^{b} $\lambda_{ex,max}$: the PL excitation maxima in THF solution or in thin film. ^{c} $\lambda_{f,max}$: the PL maxima in THF solution or in thin film. ^{d} Underlined numerical values denote absolute maxima. ^{e} Φ_f: PL quantum yields.

Pyrylium salt reactivity
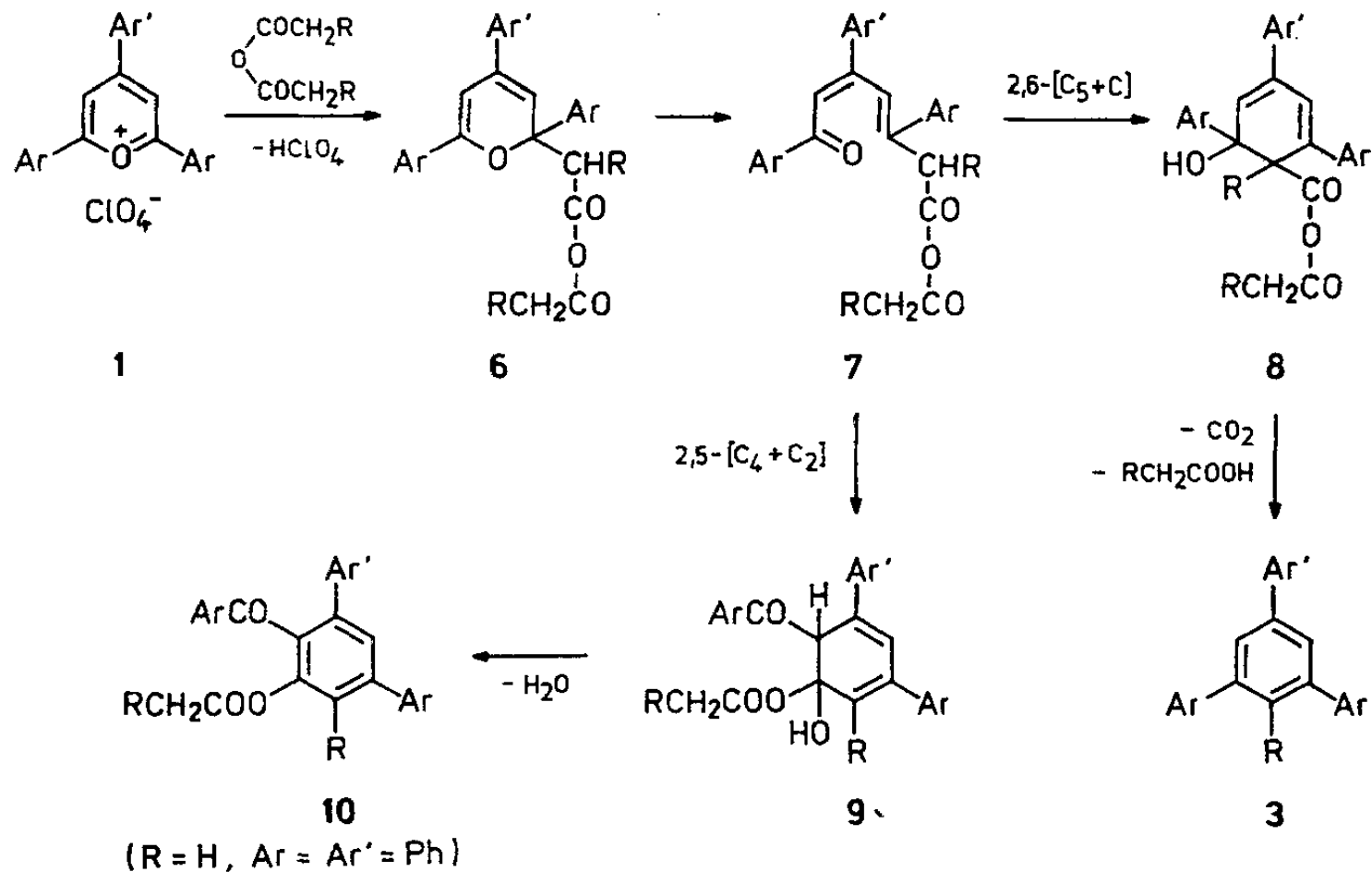
Example test questions

- The electrical resistance measured for the compressed pellet with sizes: 2cm length, 1cm diameter, formed of crystalline polyacetylene is 2000Ω.

Calculate conductivity of the material.

Is it conductor or semiconductors?

Does the conductivity should increase or decreas with grow of temperature for this sample?

Example test questions

- Polymer strongly absorb light shorter than 300nm, try to estimatate energy gap (in eV) between valency band and conduction band in this material.

1 eV = 1,602 176 6208(98) × 10^{-19} J

h = 6.626070040(81)×10^{-34} J*s = 4.135667662(25)×10^{-15} eV

$$E = h\nu = \frac{hc}{\lambda}$$

$$E = \frac{6.63 \times 10^{-34}\ Js\ 299\ 792\ 458\ m/s}{300 \times 10^{-9}\ m}$$

$$E = 6.62 \times 10^{-19}\ J$$

$$E = 4.08\ eV$$

Indigo absorb at 620 nm, is it better conductor than above polymer?

Example test questions

1. Write the mechanism of poly(phenylenevinylene) doping with $FeCl_3$.

2. What kind of quaziparticle (conjugational defects) are presented on scheme below ? Draw its structure in the case of polyacetylene.

a)   b)   c)

| cb | cb | cb |

| vb | vb | vb |