7.03.2010

Dennis

Literature Seminar

Intrinsically Conductive Polymers

Polymers

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

- **Typical properties of polymeric materials:**
  - **Strength, flexibility, elasticity, stability, mouldability, ease of handling, etc.**
- ***Combining properties of polymers with electric conductance or semiconductance open many perspectives***

Current commercial applications
based on conjugated polymers or oligomers

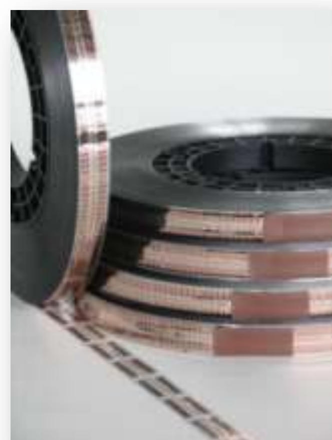
- OLED displays

Flexible lighting

Sumsung “IceTouch” MP3 Player
Transparent OLED

“Maximus” Keyboard
Each key OLED display

- Organic electronics
  - Printed electronics
  - Flexible electronics
  - Transparent



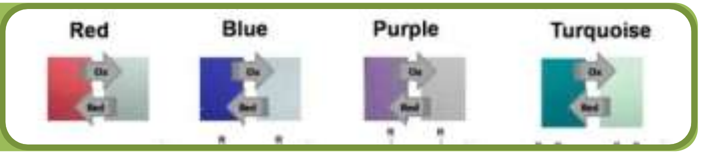
Printed Memory
from PolyIC

oe-a
Organic Electronics Association

Wide range of applications

Photovoltaic Devices (Solar Cells)

Electrochromic materials



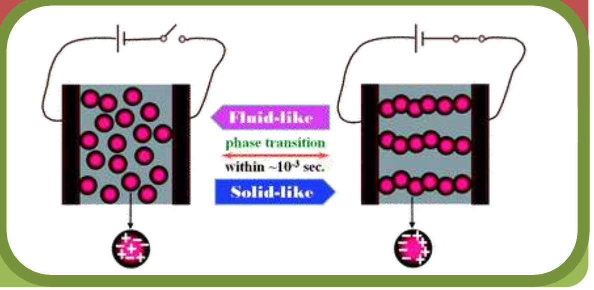
Antistatic Coating of Polymers and Glass

Artificial Muscles and Actuators

Batteries and Supercapacitors

Corrosion protection

Electrorheological materials



Nobel prize in Chemistry 2000

"for the discovery and development of electrically conductive polymers"

Alan J. Heeger ***Alan G. MacDiarmid*** ***Hideki Shirakawa***

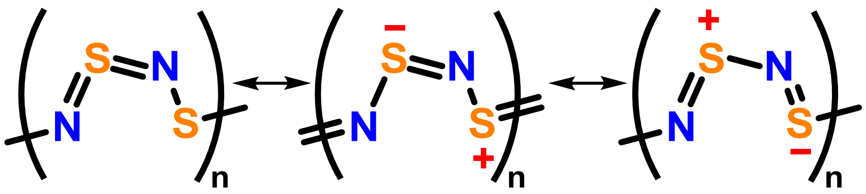
Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, $(CH)_x$

By HIDEKI SHIRAKAWA, EDWIN J. LOUIS, ALAN G. MACDIARMID,* CHWAN K. CHIANG,† and ALAN J. HEEGER†
(*Department of Chemistry and* †*Department of Physics, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia* 19104)

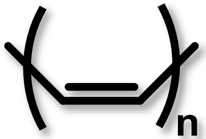
J. Chem. Soc. Chem. Comm. **1977**, 578

Some reports on conductivity of organic conjugated oligomers and polymers were presented before that

The Discovery

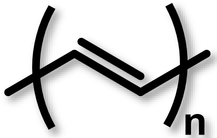


Physicist A. Heeger and chemist A. MacDiarmid collaborated to study the metallic properties of polythiazyl $(SN)_x$



all-*cis*-polyacetylene
copper colored

H. Shirakawa found efficient synthesis of all cis- and trans-polyacetylene films



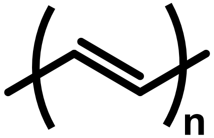
all-*trans*-polyacetylene
silver colored

But he did not investigate conductivity

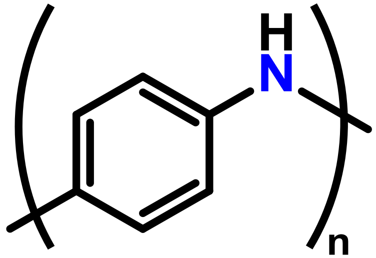
They met in Japan, started collaborating and found that:

Conductivity of oxidized by I_2("doped") *trans*-polyacetylene increased ten million times!

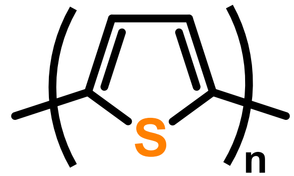
Variety of Conjugated Polymers



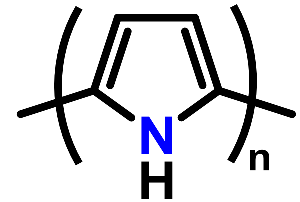
Polyacetylene
(PA)



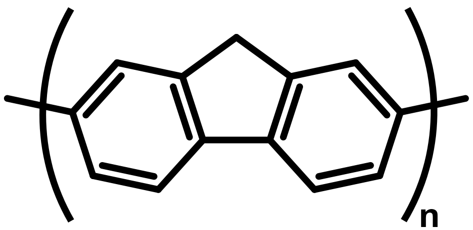
Polyaniline
(PANI)



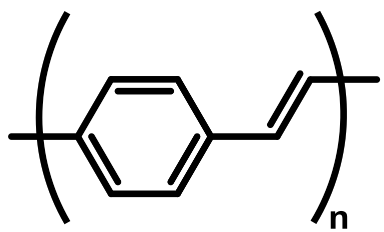
Polythiophene
(PT)



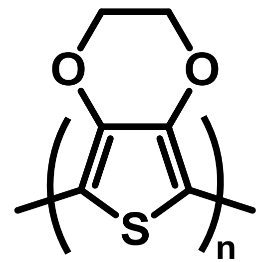
Polypyrrole
(PPy)



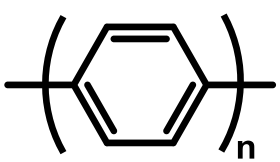
Polyfluorenes
(PF)



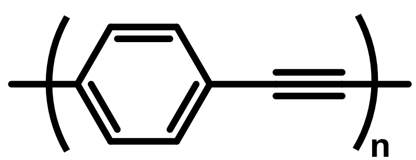
Poly(*p*-phenylene vinylene)
(PPV)



Poly(3,4-ethylenedioxythiophene)
(PEDOT)



Poly(*p*-phenylene)
(PPP)



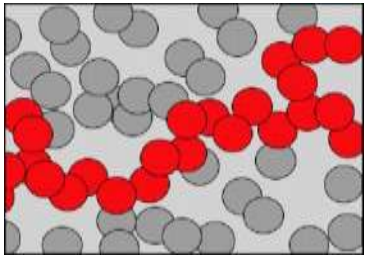
Poly(*p*-phenylene ethynylene)
(PPE)

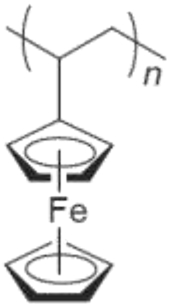
Only main backbones of conjugated polymers are presented

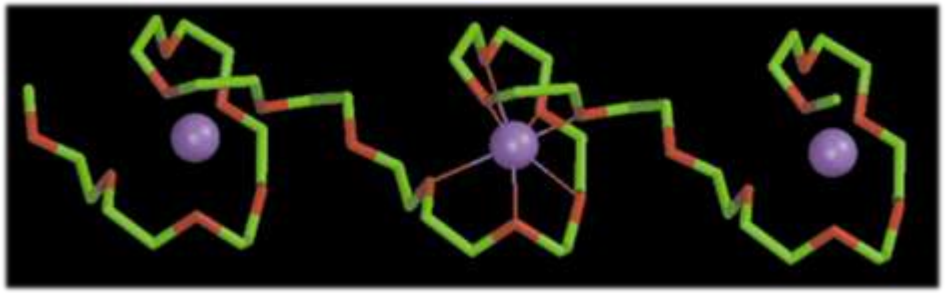
Different substitutions and copolymers were prepared

Types of conducting polymers

- **Intrinsically Conducting Polymers (ICP) – conjugated polymers**
- **Other types:**
  - Conducting Polymer Composites
    - physical mixture of a nonconductive polymer and a conducting material







poly(ethylene oxide) : $Na^{+}BPh_4^{-}$

  - Redox polymers
  - Ionically conducting polymers (Polymer electrolyte)
- Hybrid materials are also known

Electrical DC Conductivity

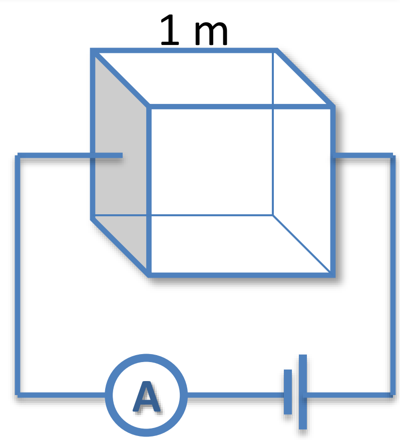
Electrical conductivity – material's ability to conduct an electric current

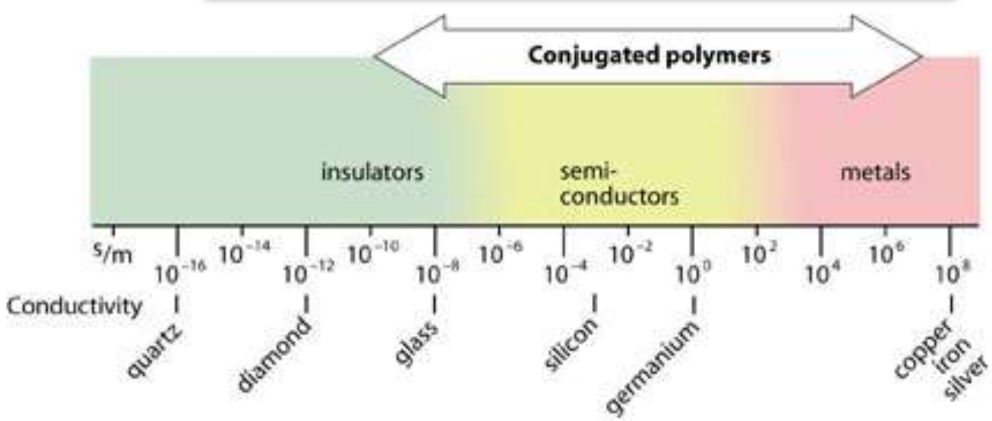
The conductivity σ is defined as the ratio of the current density **J** to the electric field strength **E** (Ohm's law)

$$\mathbf{J} = \sigma \mathbf{E}$$

SI units of σ : **siemens** per **metre** ($S \cdot m^{-1}$)
= **reciprocal of ohm** per **metre** ($\Omega^{-1} \cdot m^{-1}$)
= **mho per metre** ($\mho \cdot m^{-1}$)

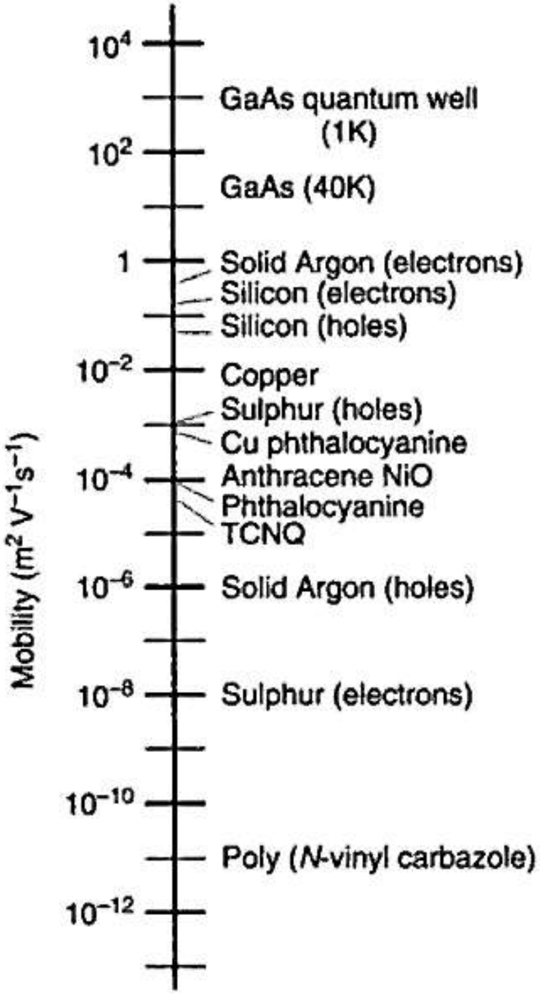
Units of J: **amperes** per **square metre** ($A \cdot m^{-2}$)
Units of E: **volts** per **metre** (Vm^{-1})





Consider a cube with edge of **1 m** and apply voltage **1 V** between two of its opposite planes. Then a current of **1 A** will flow if cube material has a conductivity of $\sigma = 1\ S \cdot m^{-1}$

Drift Mobility of the Carriers



Mobility μ characterizes the ease with which the charged species will move under the influence of the applied electric field E

The conductivity σ related to the mobility μ by

$$\sigma = q \cdot n \cdot \mu$$

q – charge

n – concentration of the charge

Used to characterize semiconducting conjugated polymers ("undoped")

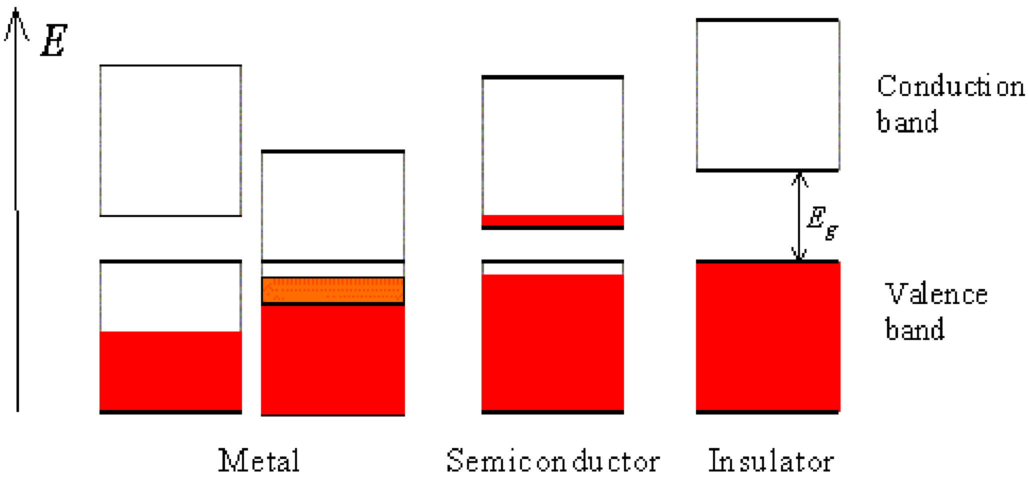
expressed as a **velocity** per **unit field** ($m^2 \cdot V^{-1} \cdot s^{-1}$)

High mobility is desired for organic electronics

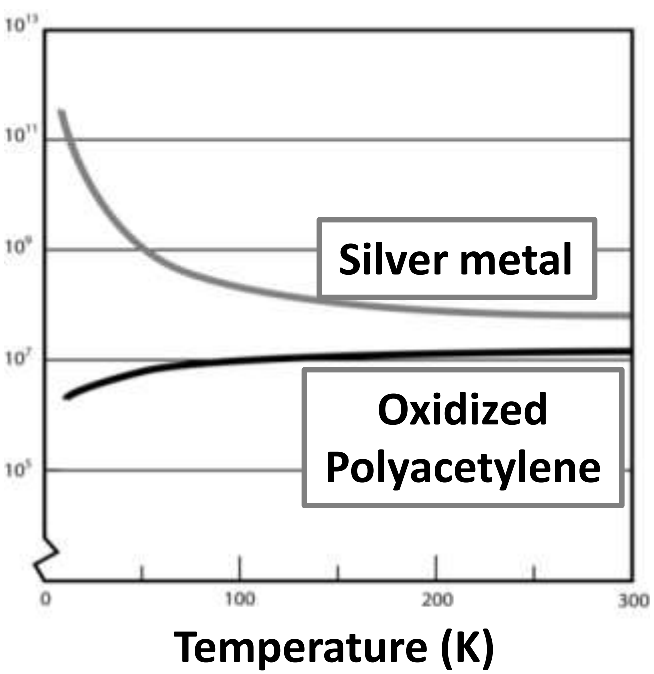
Carriers: electrons and/or holes

Insulators, Semiconductors and Conductors

Band theory in ordered state (crystal)



Energy bands consist of a large number of closely spaced energy levels



Conductivity generally increases with decreasing temperature for "metallic" materials, while it generally decreases with lowered temperature for semiconductors and insulators

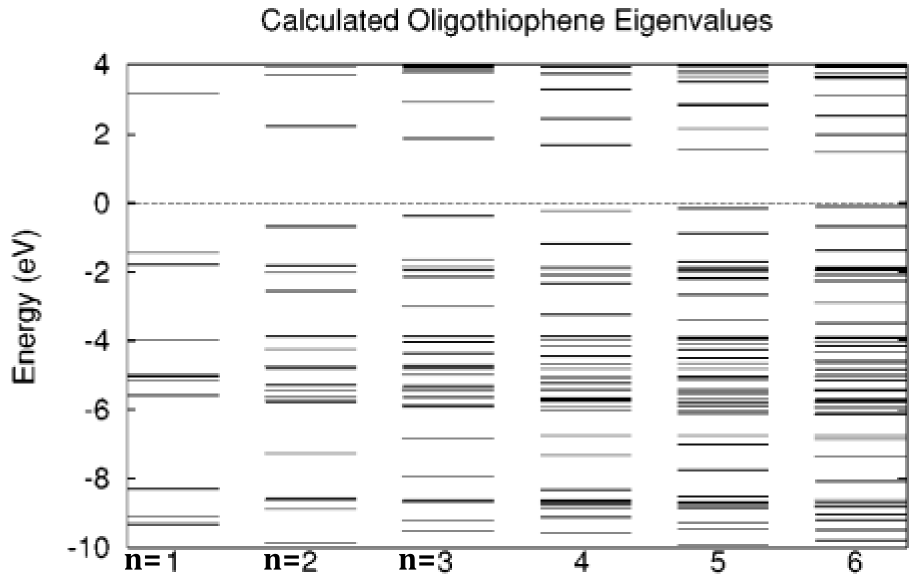
Bandgap in conjugated polymers

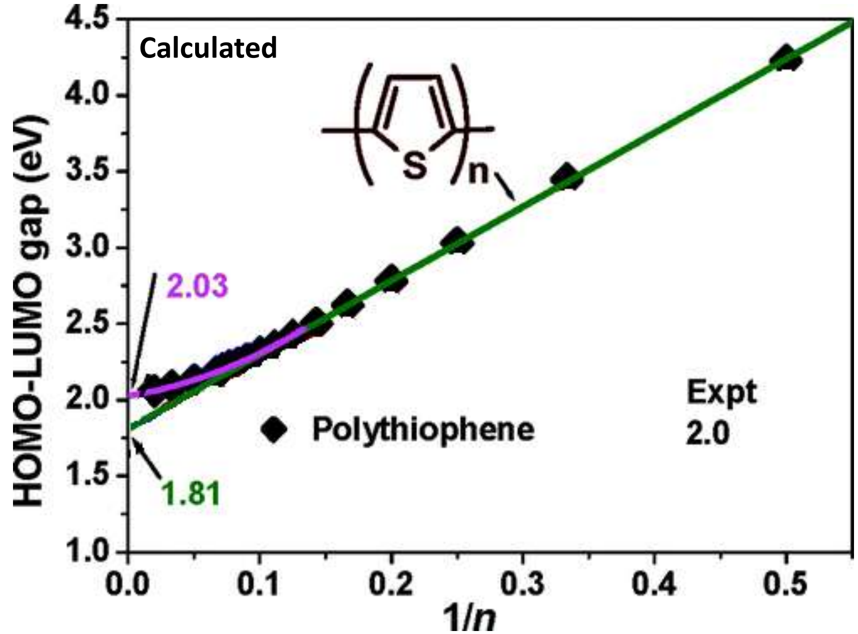
HOMO-LUMO gap (bandgap) decreases as number (*n*) of repeating units

***Conjugated polymers* are semiconductors or insulators in their non-doped state**

Decrease is Proportional to 1/*n* up to *n*≈10

Development of energy bands



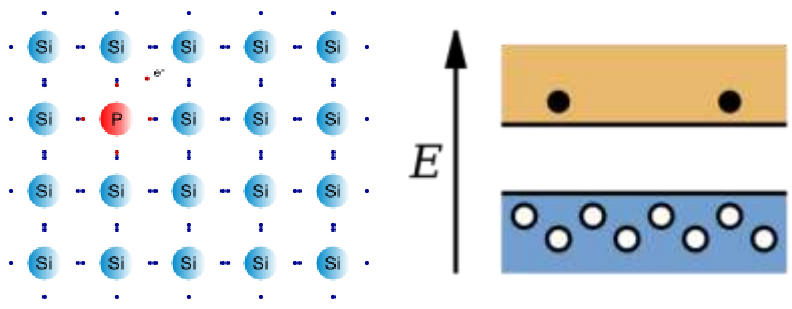


Marks et al., *Phys. Rev. B* **2003**, *68*, 035204
Bendikov et al., *Org. Lett.* **2006**, *8*, 5243

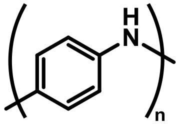
Doping principle

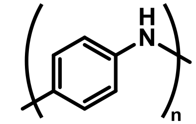
- Conjugated polymers
  - Transfer of the charge to or from π-system
  - Introduced chemically or electrochemically
    - Oxidation – p-doping
    - Reduction – n-doping
  - Doping is high 1% - 40%
  - Changes in geometry

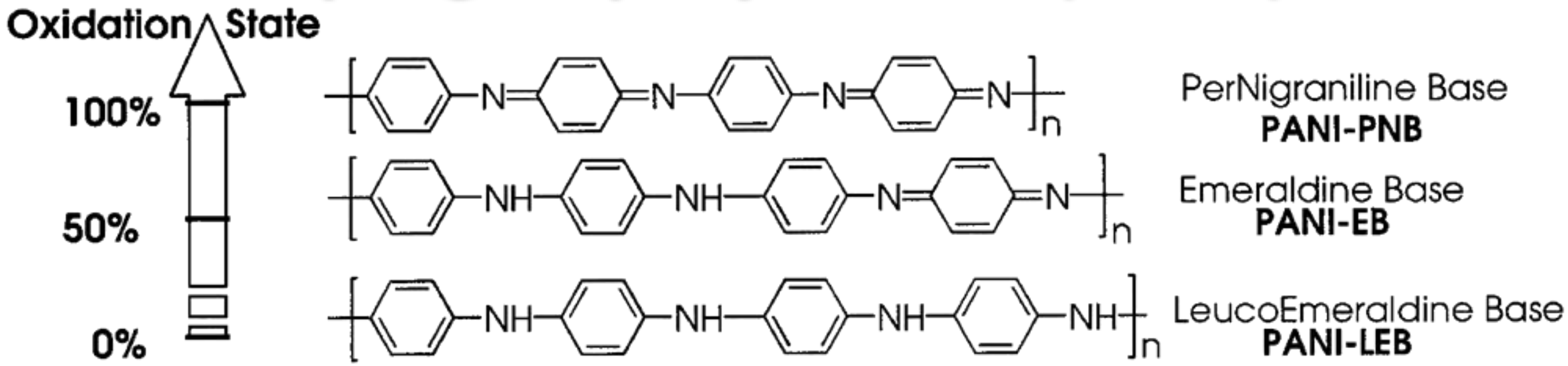
- "Regular" semiconductors (extrinsic)
  - Introduced to lattice
  - Doping is small <0.1%
  - No changes in geometry of lattice



Doping of polyaniline (PANI)

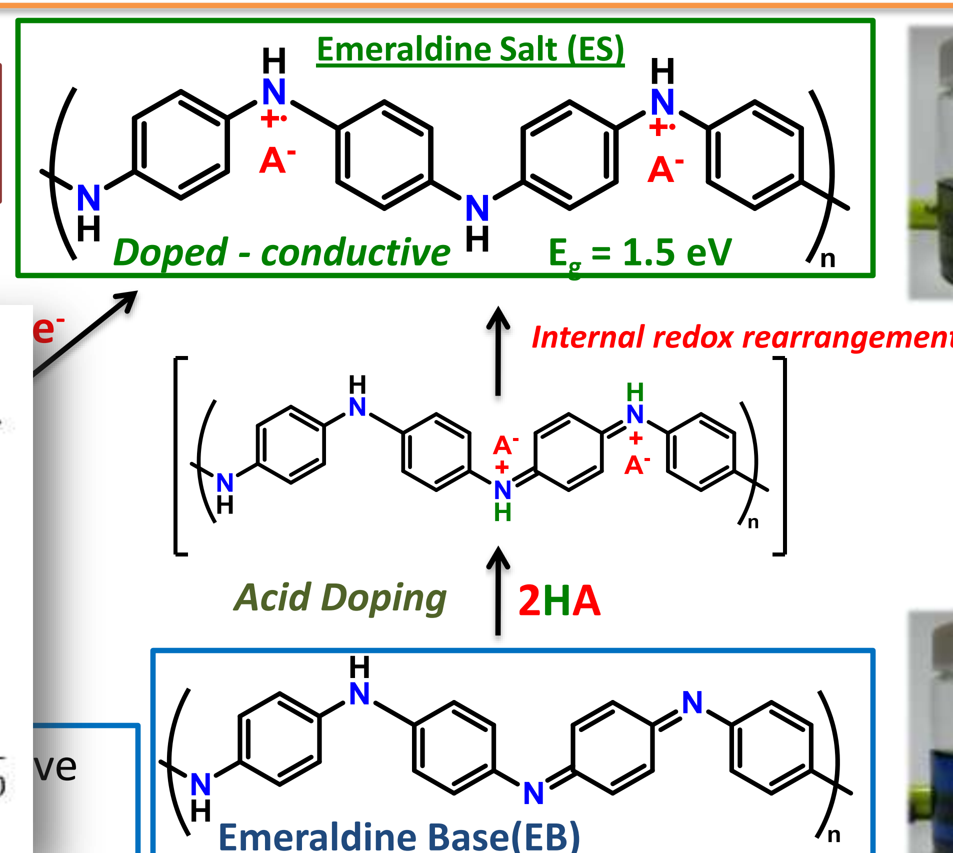


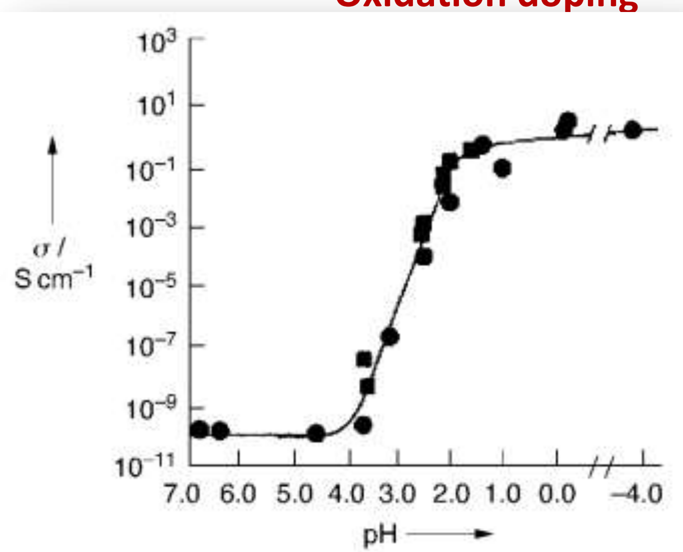




Cation-radicals (Polarons)
poly(semiquinone) radical

Oxidation doping



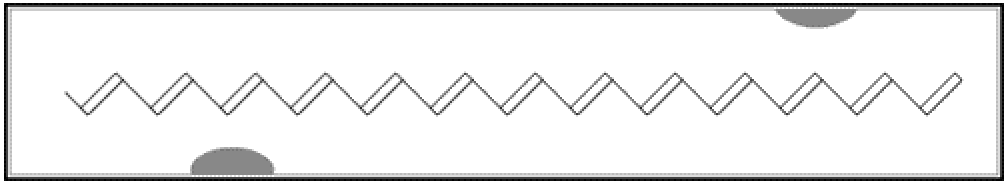


Conduction in polymers

The overall mobility of charge carriers in conducting polymers depends on two components

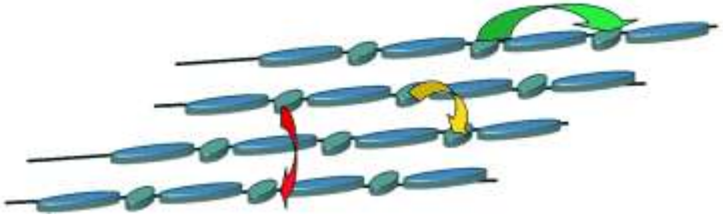
- **Intra**chain mobility

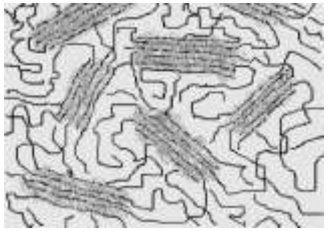
  charge transfer along the polymer chain



- **Inter**chain mobility

  hopping *or* ***tunneling*** *of the charge between chains or crystalline regions*





Interchain hopping

Temperature dependence of DC conductivity helps in determination of charge transport mechanism

For example some models

Arrhenius-like character

Crystalline semiconductors

Band conduction mechanism

$$\sigma = \sigma_0 e^{-\left(\frac{E_a}{kT}\right)}$$

Mott's Variable-Range-Hopping (VRH)

Amorphous semiconductors

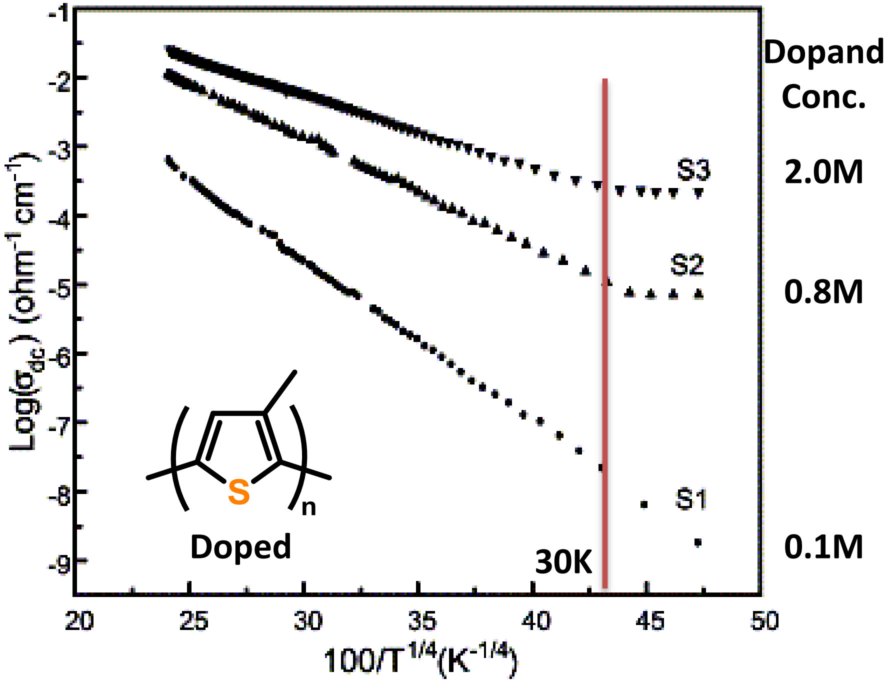
Hopping conduction mechanism

When randomness in inter-chain distance is present, i.e., isotropic system

$$\sigma = \sigma_0 e^{-\left(\frac{T_0}{T}\right)^{\alpha}}$$

1D: $\alpha = ½$
3D: $\alpha = ¼$

Mechanism of DC conduction in ferric chloride doped poly(3-methyl thiophene)



Conductivity is the sum of hopping and tunneling mechanisms

Singh et al., *Curr. Appl. Phys.* **2003**, *3*, 235

Stability and Processability

What do we want from polymer?

- **Solubility (non-doped and doped)**
- **Environmental stability**
- **Thermal stability**
- **Electronic properties**

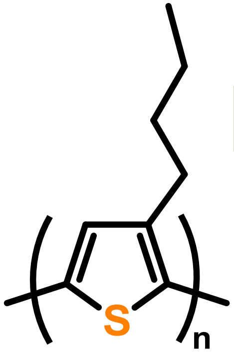
STABILITY AND PROCESSING ATTRIBUTES OF SOME CONDUCTING POLYMERS

POLYMER	CONDUCTIVITY (Ω^{-1} cm^{-1})	STABILITY (doped state)	PROCESSING POSSIBILITIES
Polyacetylene	10^3 - 10^5	poor	limited
Polyphenylene	1000	poor	limited
PPV	1000	poor	limited
Polypyrroles	100	good	good
Polythiophenes	100	good	excellent
Polyaniline	10	good	good

Techniques that can be used:

- **Substitution on polymeric backbone**
- **Counter-ion induced processability**
- Colloidal dispersions
- Copolymers

Soluble poly(3-alkylthiophene) PAT

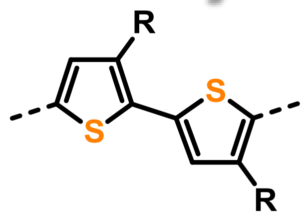


Elsenbaumer 1986

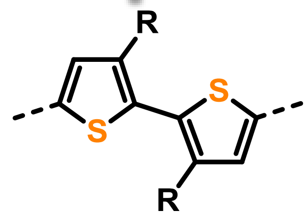
Soluble in organic solvents

Lower conductivities (up to 5 S/cm)

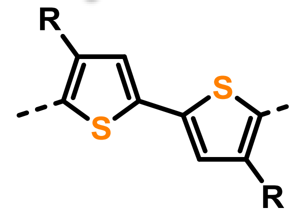
Due to regioirregularity
(only 50-80% HT couplings)



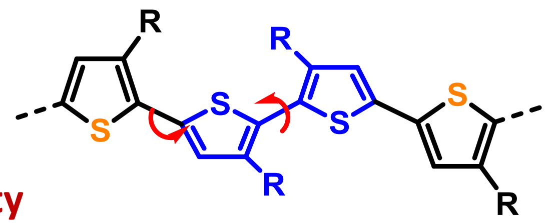
Head-to-Tail (HT)



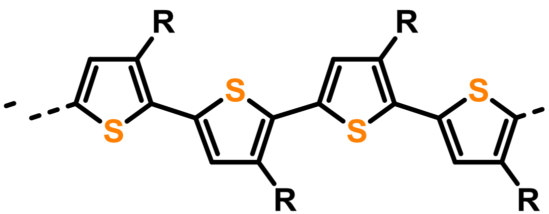
Head-to-Head (HH)



Tail-to-Tail (TT)

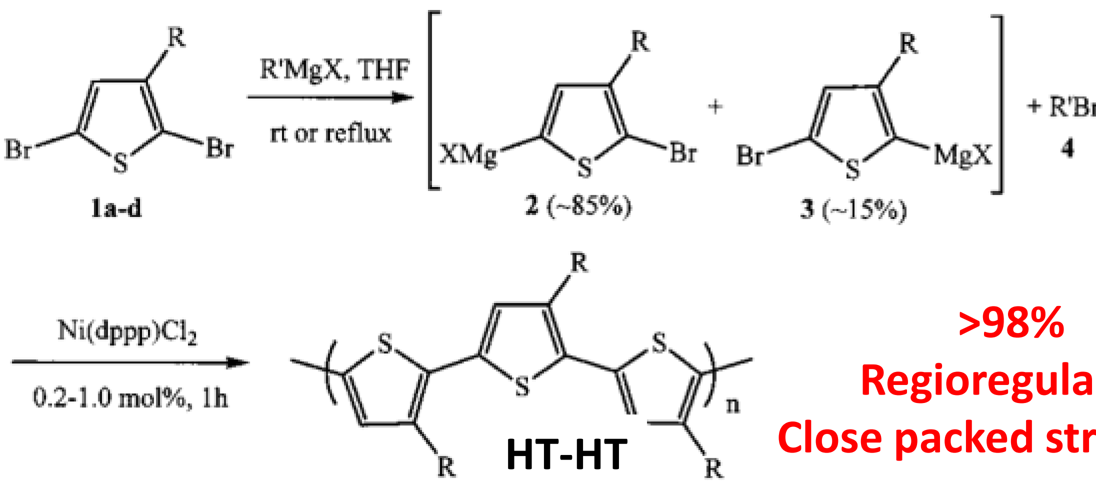


Regio*ir*regular HT-HH-TT



Regioregular HT-HT-HT

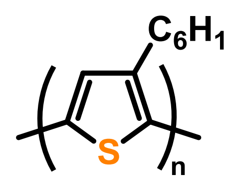
Synthesis of regioregular PATs by Grignard metathesis Method (GRIM) by McCullough



yield 70%

>98%
Regioregularity
Close packed structures

M_n: 20–35 kDa with PDI: 1.2–1.4
Conductivities up to 1000 S/cm

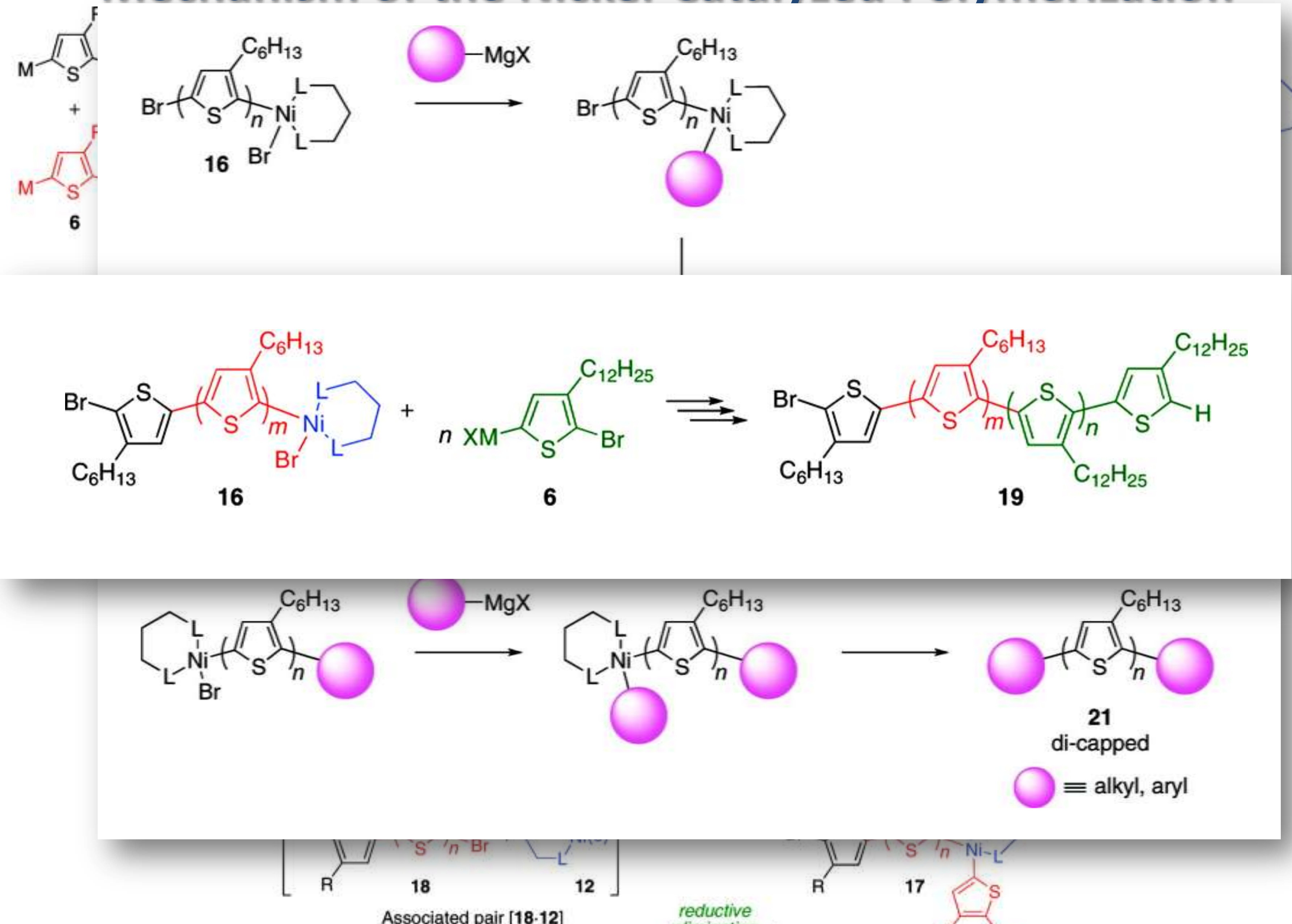


poly(3-hexylthiophene)
rrP3HT
Mobility 0.2 $cm^2V^{-1}s^{-1}$

(>100 papers in 2010)

McCullough et al., *Macromolecules* **2001**, *34*, 4324

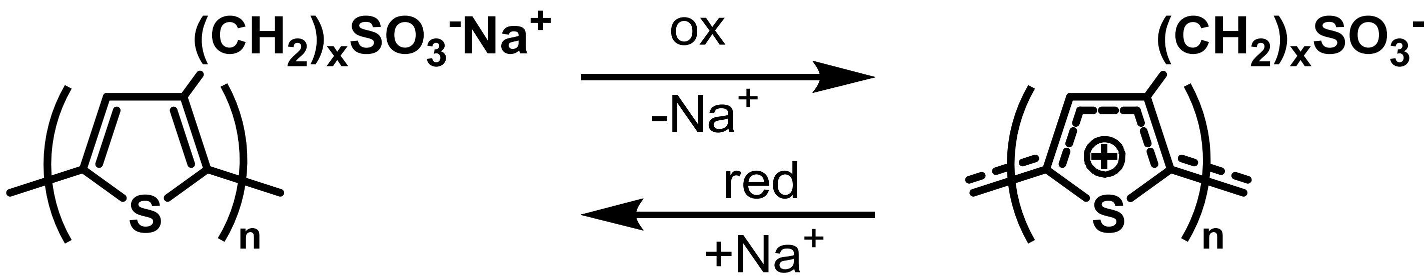
Mechanism of the Nickel-Catalyzed Polymerization



McCullough et al., *Chem. Res.* **2008**, *41*, 1202

Self-doping

In 1987 Wudl et al. proposed concept of self-doping, where
the counterions are covalently bound to the polymer backbone
in order to increase solubility in water and migration rate of the counterions



x = 2 or 4

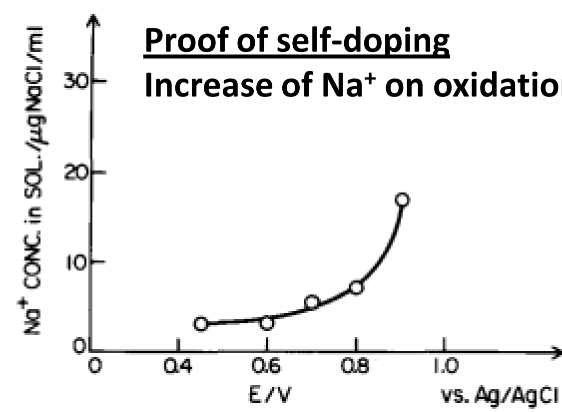
10^{-2} S/cm

10 S/cm ($NOPF_6$)

First *water-soluble conducting polymers*

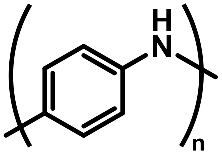
Mechanism of self-doping involves the Na^+ "popping"

in contrast to regular polymers where
anions are incorporated to the backbone

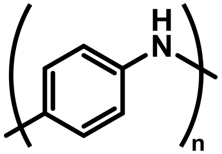


Proof of self-doping
Increase of Na^+ on oxidation

Wudl et al., *J. Am. Chem. Soc.* **1987**, *109*, 1858
Wudl et al., *Synth. Met.* **1987**, *20*, 151



Polyaniline (PANI)



- Oxidation of aniline was studied from 19 century
  - Fritzsche in 1840 observed the appearance of a blue color during the aniline oxidation
  - Aniline – means “indigo”, “deep-blue”
  - First conductivity report by Buvet in 1967
- From mid-1980s most studied among the conducting polymers
- Easy synthesis in aqueous media, in a variety of different morphologies
- Many applications:
  - Molecular sensors
  - Rechargeable batteries
  - Antistatic coating
  - Non-volitale memory

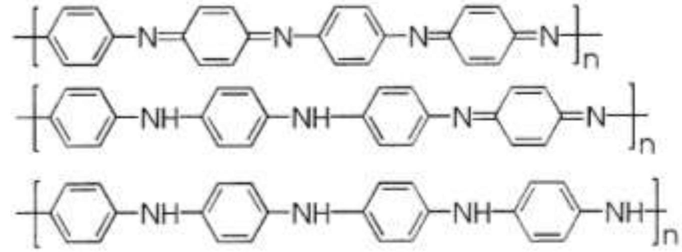
"Standard" Synthesis

Exists in different oxidation states

Reactive ->

Stable in air ->

Reactive ->

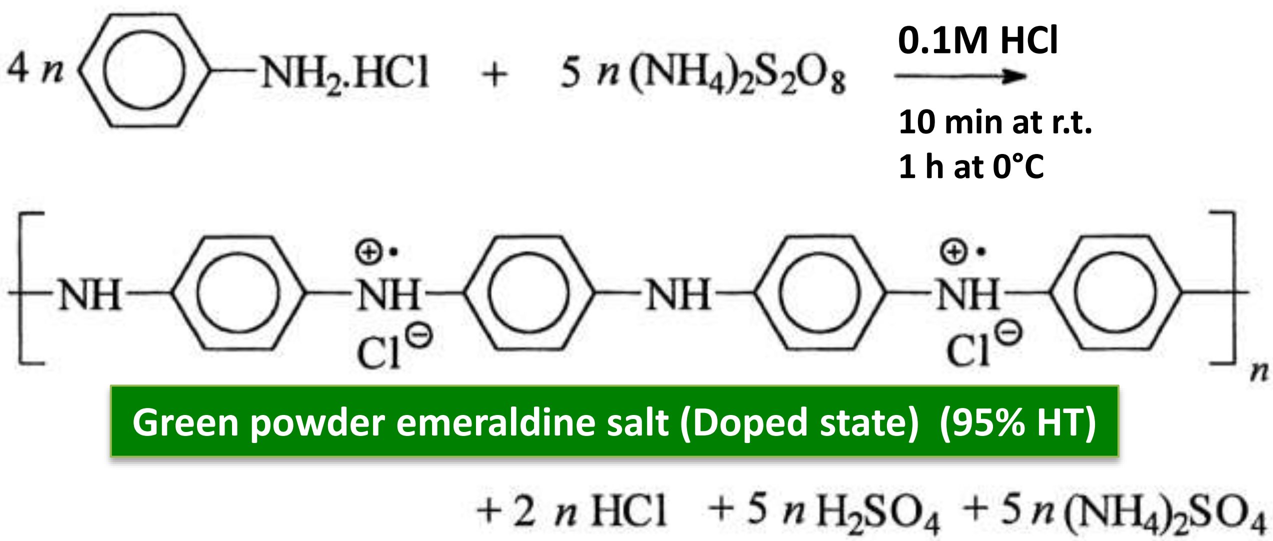


PerNigraniline Base **PANI-PNB**

Emeraldine Base **PANI-EB**

LeucoEmeraldine Base **PANI-LEB**

Most used simple chemical synthesis of PANI via oxidative polymerization by peroxydisulfate



$$4n\ C_6H_5NH_2{\cdot}HCl + 5n\ (NH_4)_2S_2O_8 \xrightarrow{0.1M\ HCl} \ldots + 2n\ HCl + 5n\ H_2SO_4 + 5n\ (NH_4)_2SO_4$$

Green powder emeraldine salt (Doped state) (95% HT)

Heterogeneous polymerization

Conductivities (dopping with HCl) are in range 2-10 S/cm

M_w: up to 350 000 (usually 30 000) Da

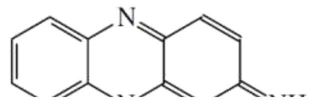
PDI: from >1 to 6 (usually 2.2-2.4)

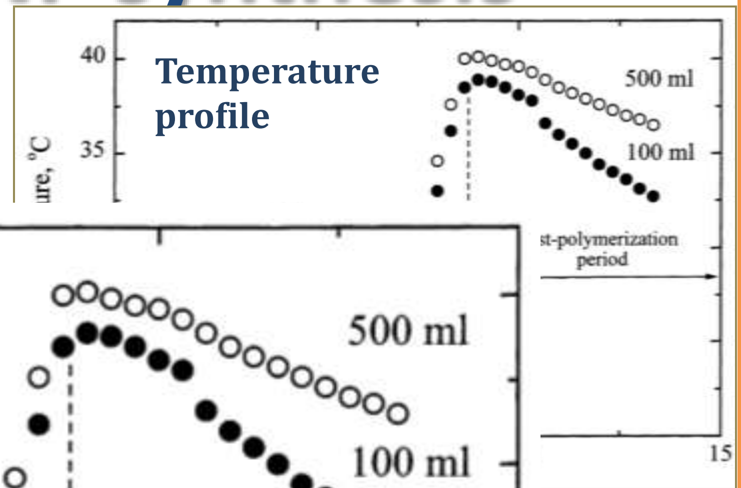
MacDiarmid and Manohar et al., *J. Am. Chem. Soc.* **2005**, *127*, 16770

Mechanism of PANI synthesis

Heterogeneous polymerization

Phenazine nucleate





1) Initiation

Nucleation :
under ind
(Non-solu

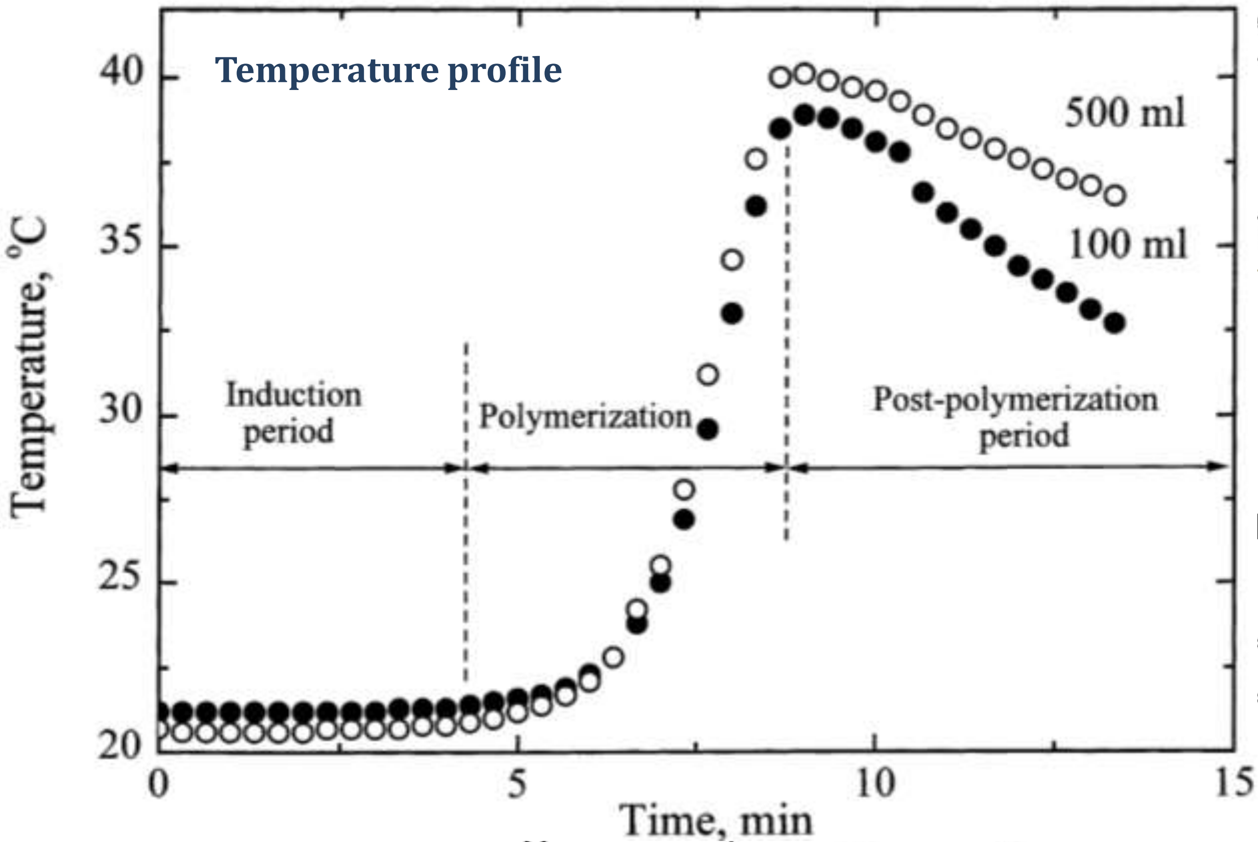
2) Propagation

Growing PA
protonate
(pernig

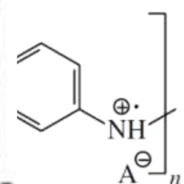
Redox is ass
p

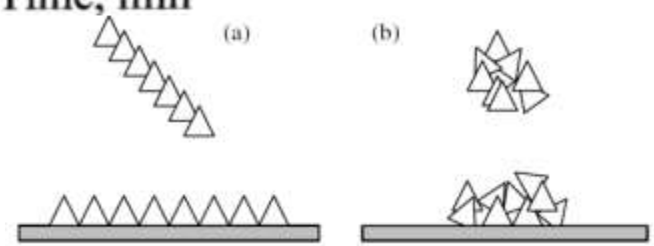
3) Terminatior

Hydroly



h



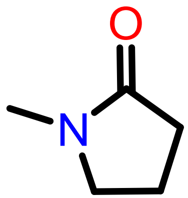


I. Sapurina, J. Stejskal, *Polym. Int.* **2008**, *57*, 1295

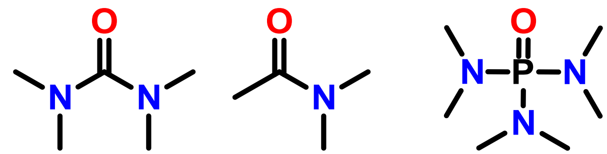
Solubility of PANI

EB is difficult to dissolve due to interchain hydrogen bonds

most used solvent



NMP
N-methyl-2-pyrrolidinone



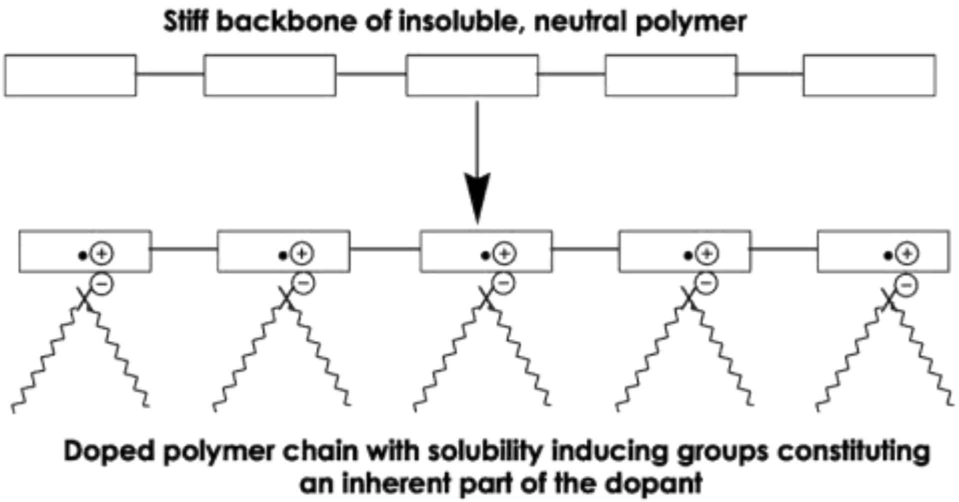
TMU DMAc HMPA

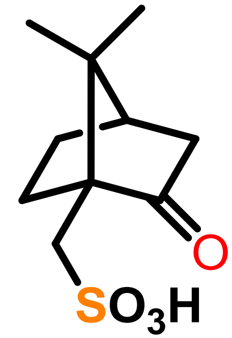
Convenient processing of conductive polymers demands solubility in doped form

- EB soluble (20 w%) in H_2SO_4 (97%) resulting in doped state ES
  - fibers with high crystallinity have showed high conductivity 20-60 S/cm
  - not practical for film casting

How one can induce solubility of doped form without modifying the polymers ?

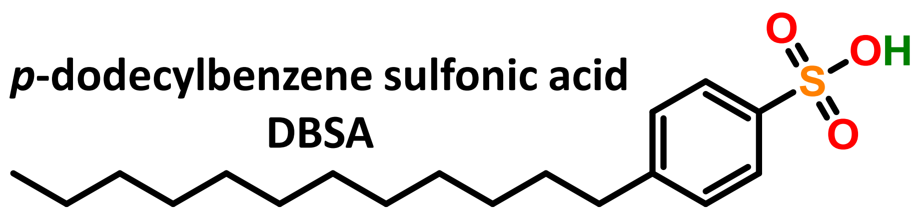
Counter-ion induced processability





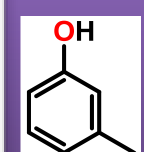
Camphorsulfonic acid
CSA

***p*-dodecylbenzene sulfonic acid**
DBSA



PANI doped with these acids is soluble in organic solvents,
e.g., xylene, chloroform, *m*-cresol , DMSO

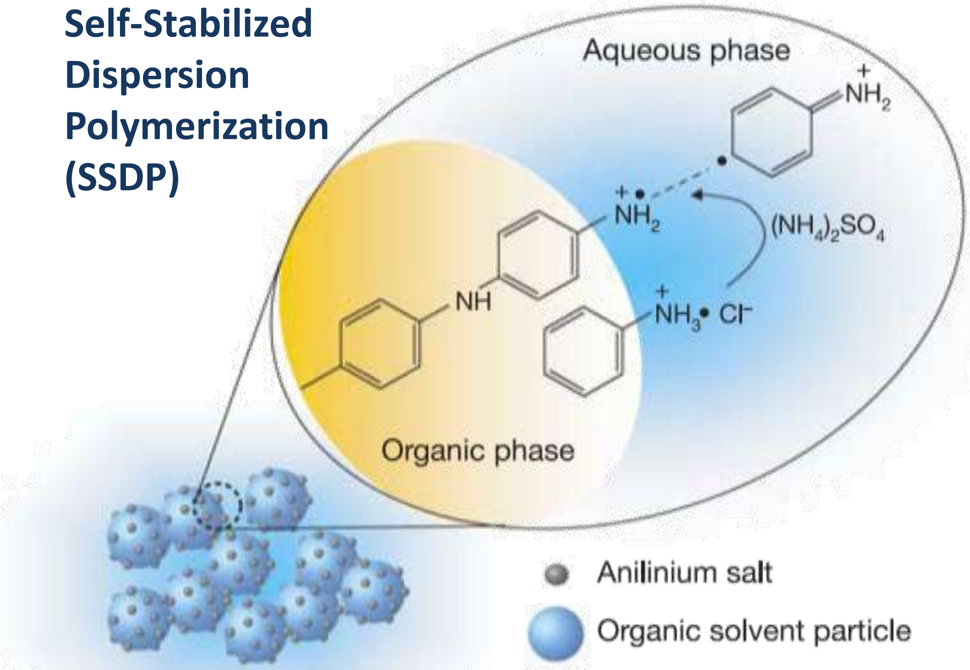
Films casted from *m*-cresol shows conductivities 1000 times larger than films casted from chloroform
"Secondary doping"



Heeger et al., *Synth. Met.* **1992**, *48*, 91
Epstein et al., *Chem. Mater.* **2002**, *14*, 1430

Metallic transport in polyaniline

Self-Stabilized Dispersion Polymerization (SSDP)



2:1 (v/v) water:chloroform

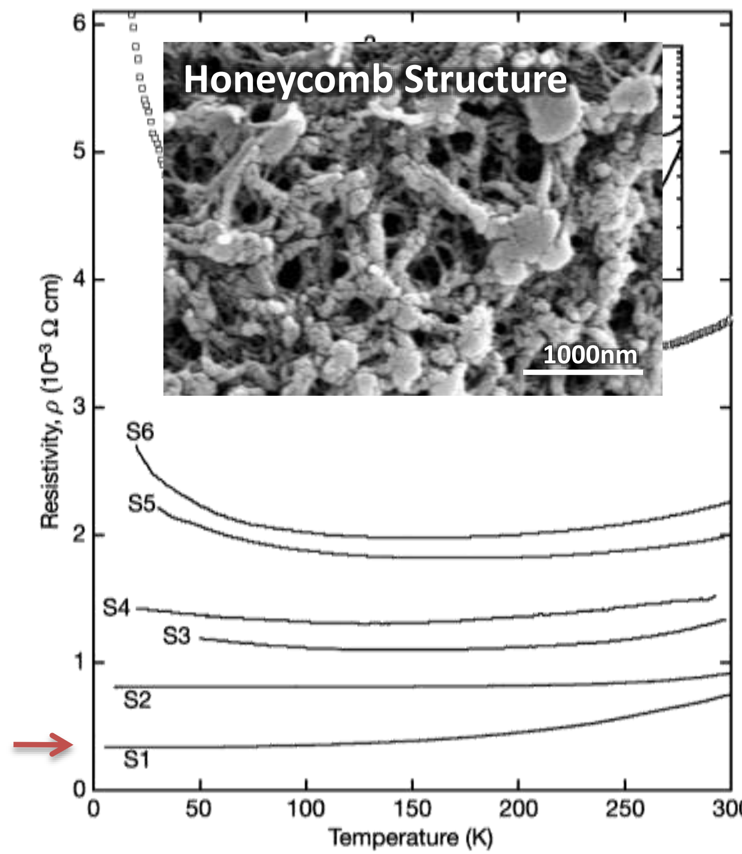
agitator mixed at 200 rpm

Heterogeneous biphasic polymerization, where surfactant is the aniline salt

Reaction at -35°C: M_w = 53 000 Da ; PDI = 2.5

Doped with CSA and casted from m-cresol

Resistivity (1/σ) vs. Temperature



S1 shows true metallic behavior

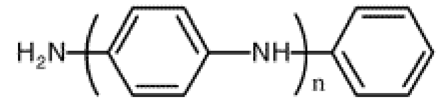
Conductivity at 300K is 1300 S/cm

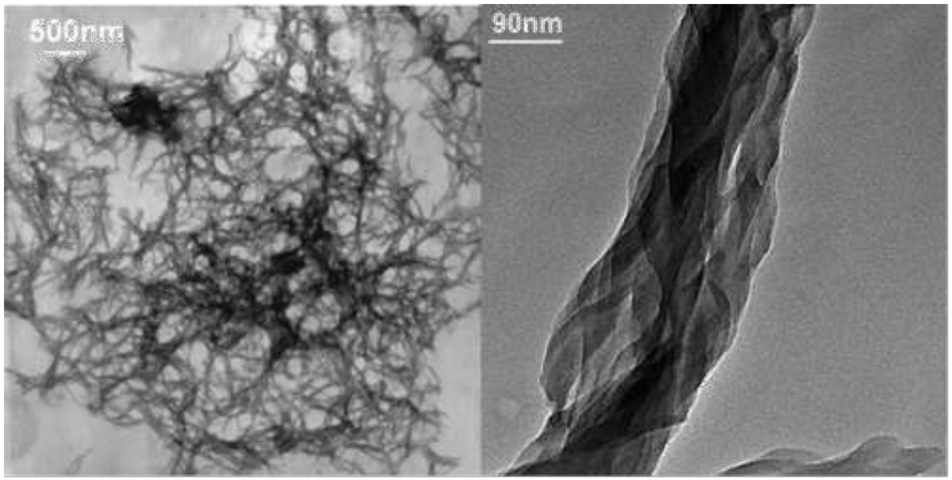
First example of metallic conductance

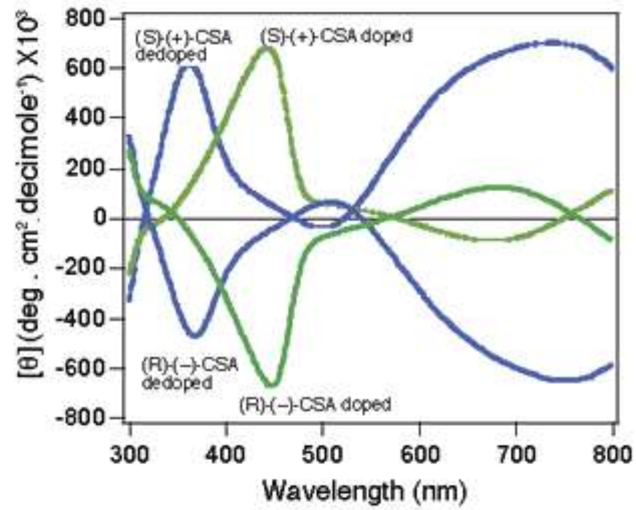
Lee et al., *Nature* **2006**, *441*, 65
Lee et al., *Adv. Funct. Mater.* **2005**, *15*, 1495

Polyaniline Nanofibers

Synthesis in concentrated (+)-CSA or (-)-CSA
and addition of oligomers produces **chiral nanofibers**



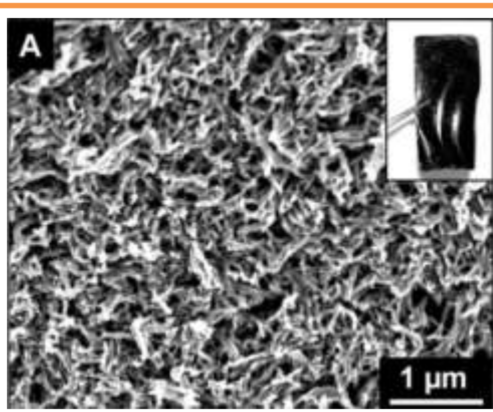


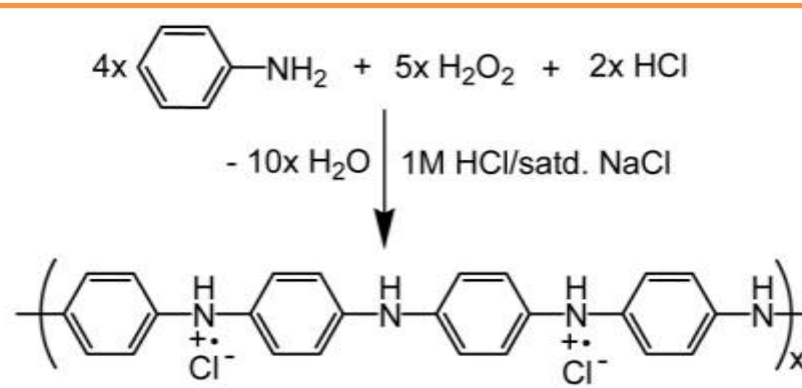


Wang et al., *J. Am. Chem. Soc.* **2004**, *126*, 2278

Catalyst-Free Synthesis of Oligoanilines and Polyaniline Nanofibers Using H_2O_2

60–80 nm diameter nanofibers

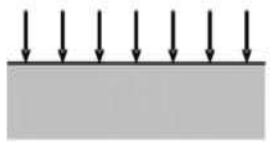




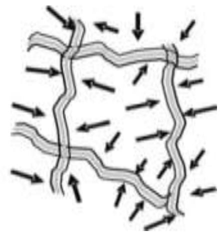
Manohar et al., *J. Am. Chem. Soc.* **2009**, *131*, 12528

Polyaniline nanofibers for chemsensors

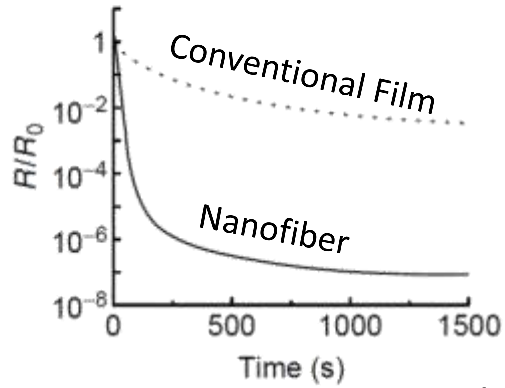
- Useful in chemical sensors since have large surface area per unit mass and much greater penetration depth



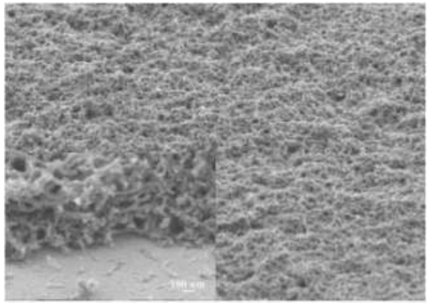
Conventional Film

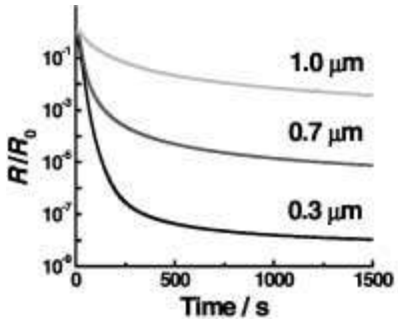


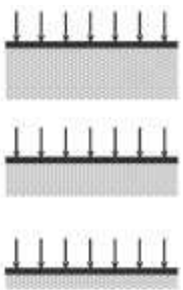
Nanofiber Film

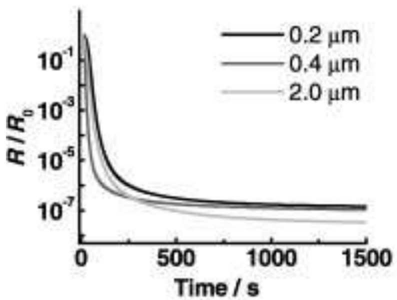


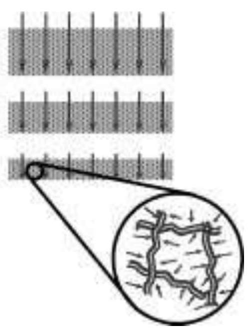
Response to 100ppm HCl





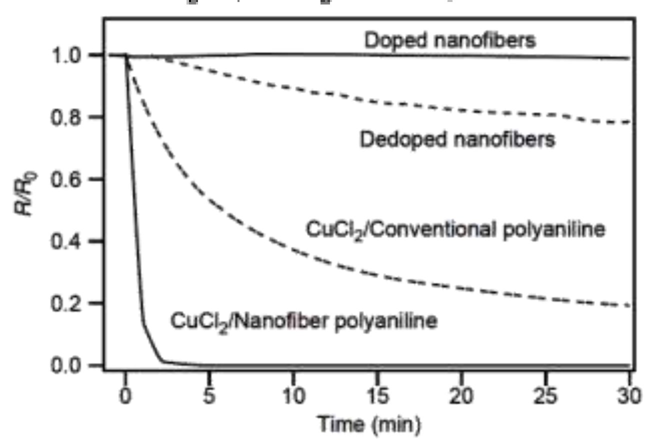






Metal composite

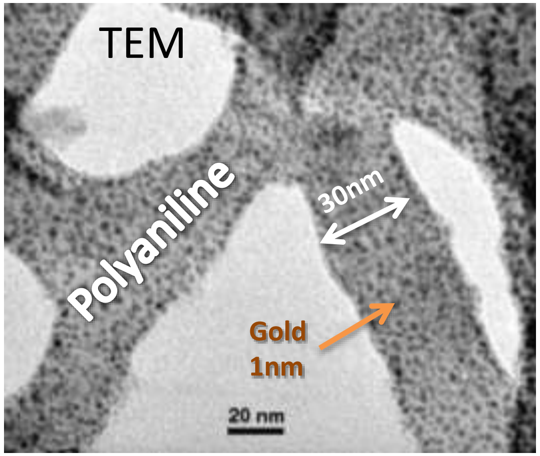
$$H_2S + MCl_2 \rightarrow MS + 2\,HCl$$

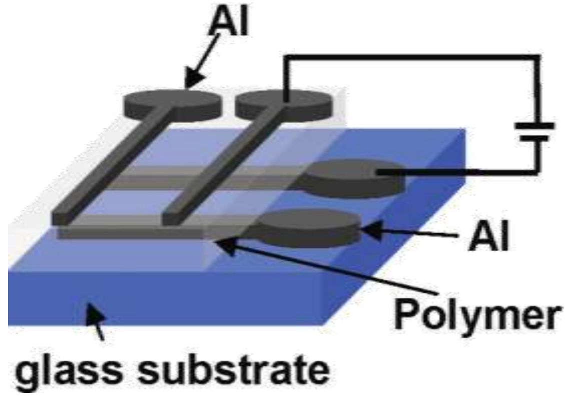


Response to 10ppm H_2S

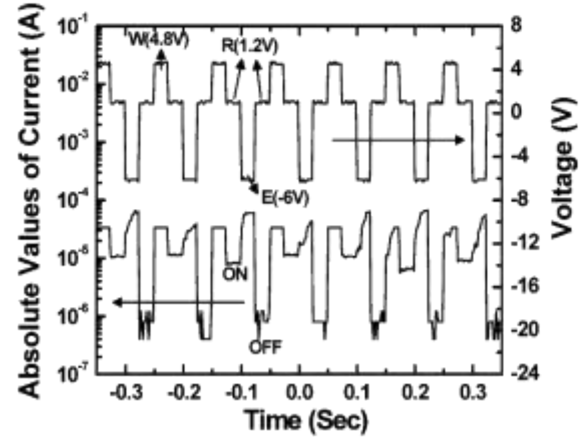
R. B. Kaner et al., *Chem. Eur. J.* **2004**, *10*, 1314; *Small* **2005**, *1*, 624.

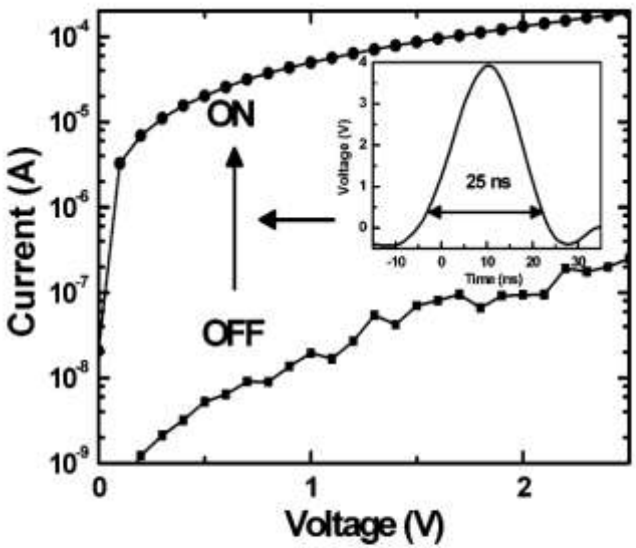
Polyaniline Nanofiber/Gold Nanoparticle Nonvolatile Memory



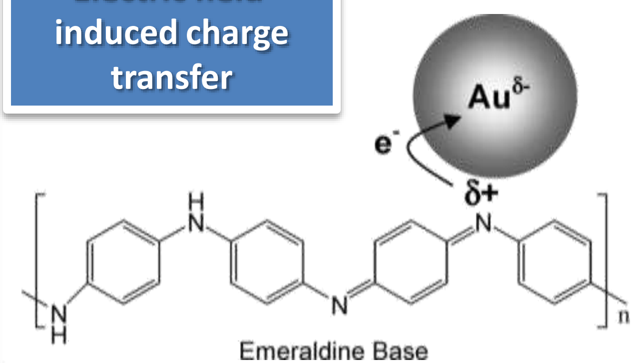


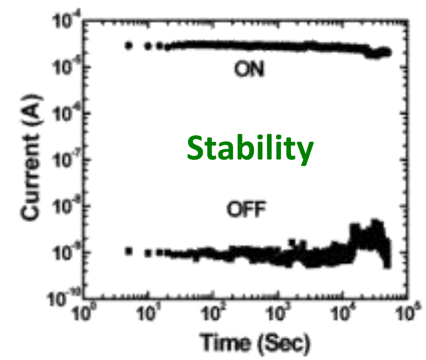
0.2 x 0.2 mm^2





Electric field-induced charge transfer

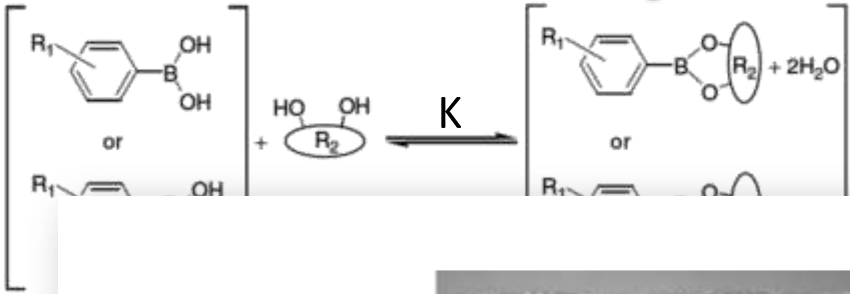


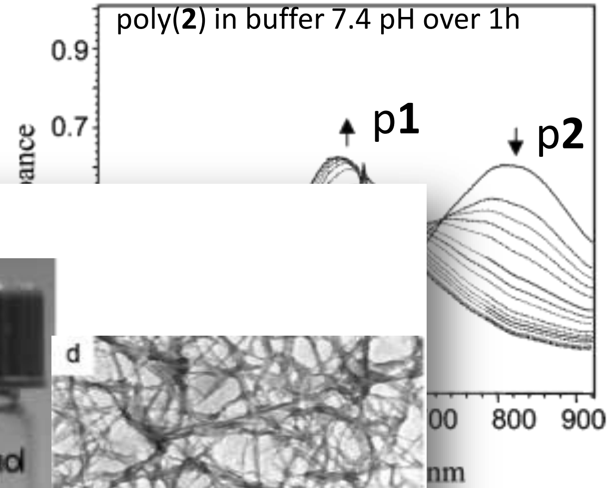


The nanosecond transition time - switching is due to electronic processes rather than chemical reactions, conformational changes or isomerizations

R. J. Tseng, J. Huang, J. Ouyang, R. B. Kaner, Y. Yang, *Nano Letters* **2005**, 5, 1077

Boronic Acid Substituted Self-doped Polyaniline (PABA)





Lewis

Ch

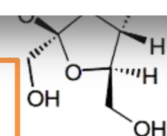
HO-

3-amir

luble
y(1)
lf-doped
ate

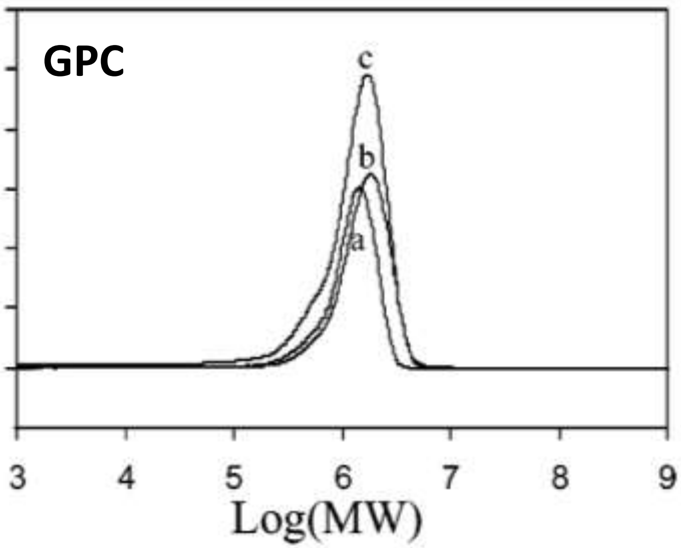
no polymerization without at least one equivalent of fluoride

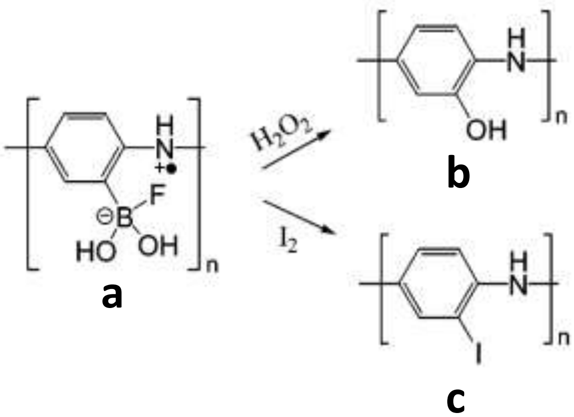
Soluble poly(2)
Self-doped state



Freund et al., *J. Am. Chem. Soc.* **2003**, *126*, 52; *Macromol. Chem. Phys.* **2008**, *209*, 1094.

Molecular weight of PABA



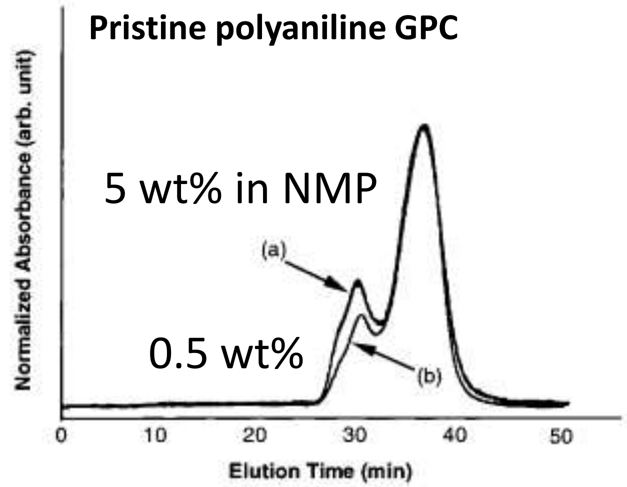


High molecular weight observed for PABA is not due to boronic acid anhydride cross-linking

Unimodal molecular weight distribution
M_w = 1,760,000 Da; PDI = 1.05

High molecular weight results from its solubility

Lower conductivity than PANI
0.96 S/cm

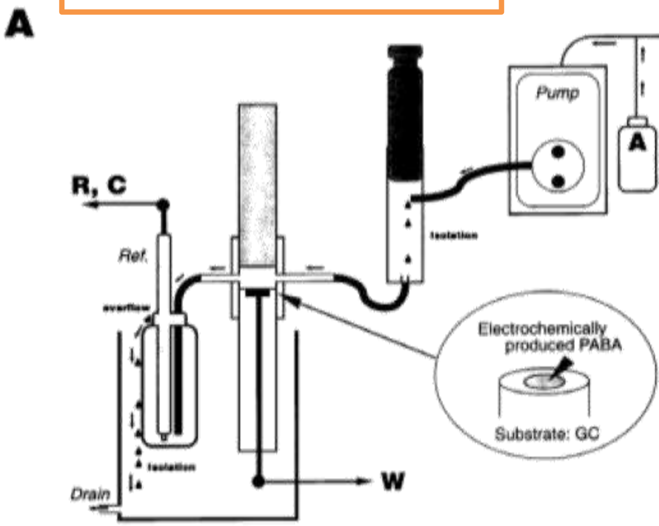


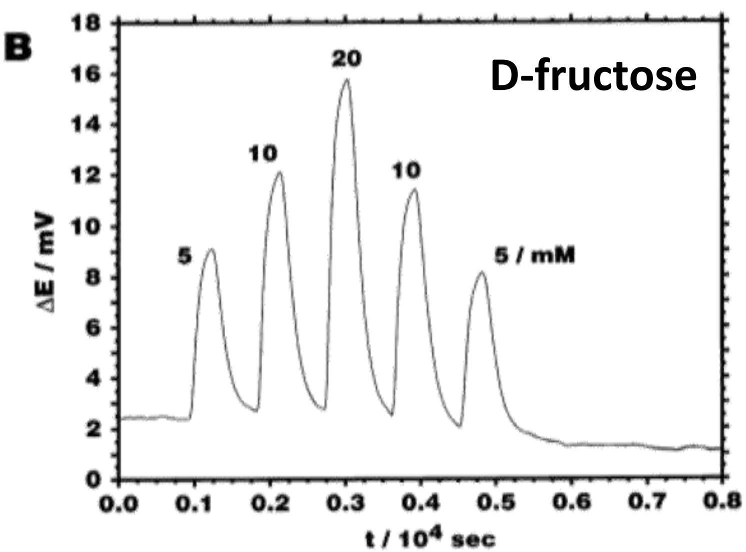
Epstein and MacDiarmid et al., *Macromolecules* **1997**, *30*, 7634

Freund et al., *Macromolecules* **2005**, *38*, 10022

Sensor applications

Saccharide sensor

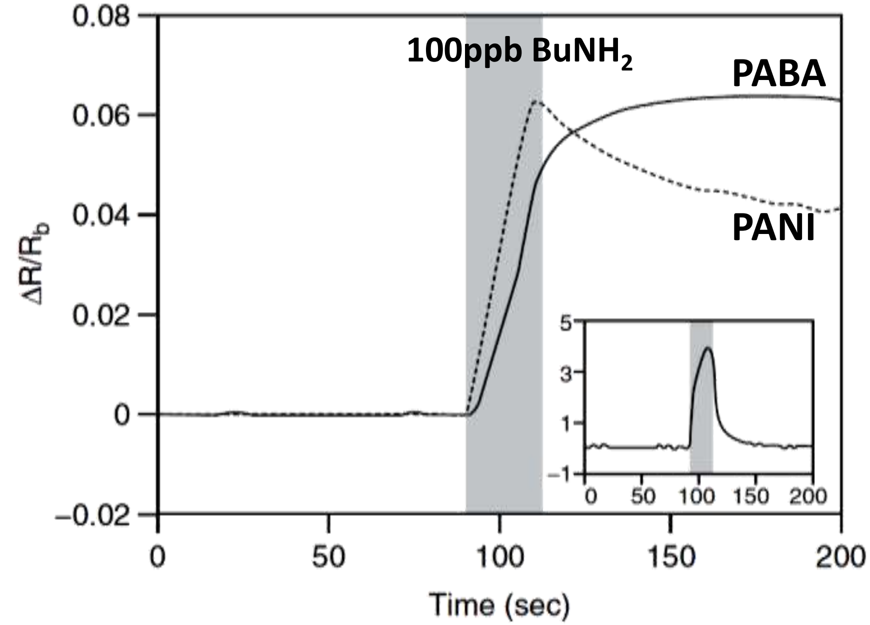


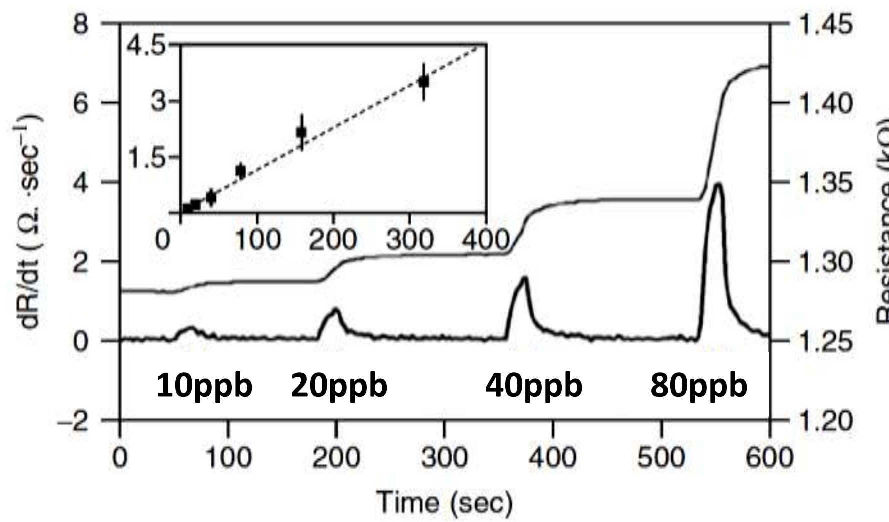


NAD+/NADH response was also reported

Freund et al., *J. Am. Chem. Soc.* **2002**, *124*, 12486

Biogenic amine vapour detection





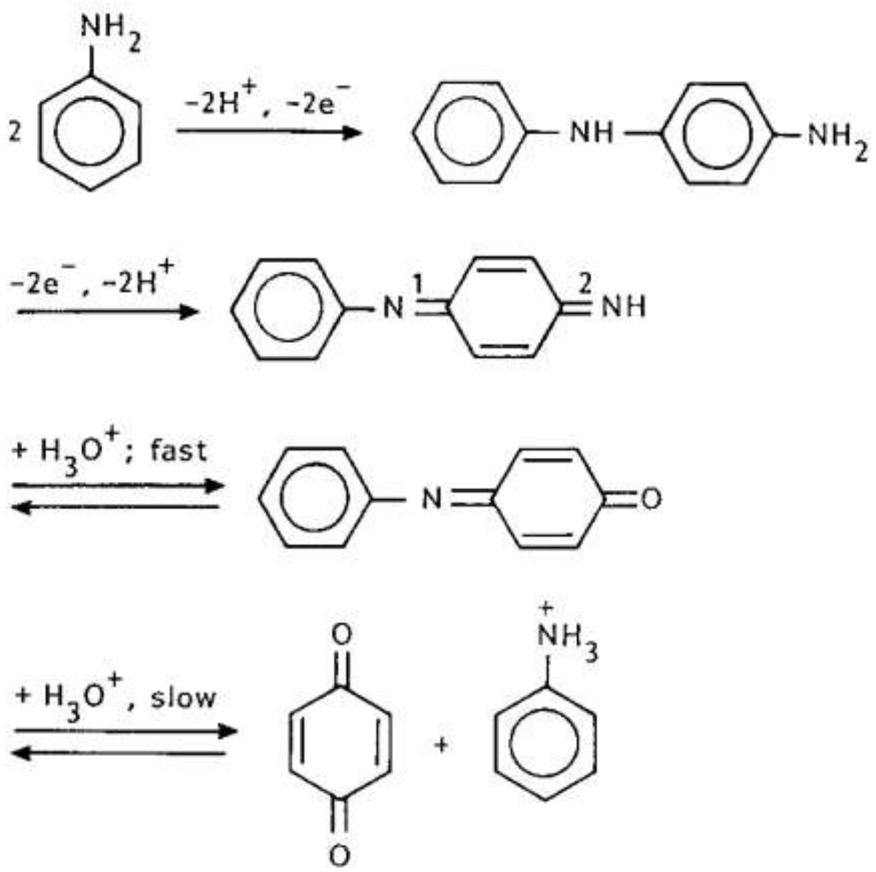
Conclusions

- Fast growing field
- Only small part of it was presented
- There is a lot to do both theoretically and practically
- Polymer properties can be tailored by organic chemistry
- Applications will change our lifestyle

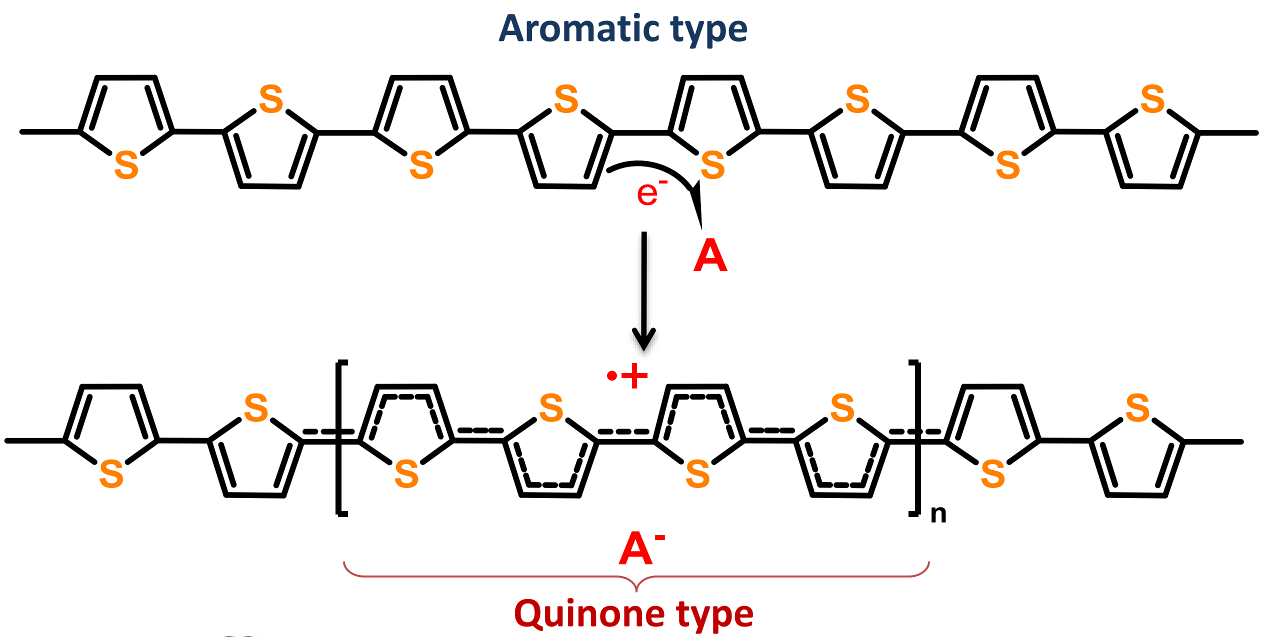
Thank you!

This page intentionally left blank

Termination step PANI

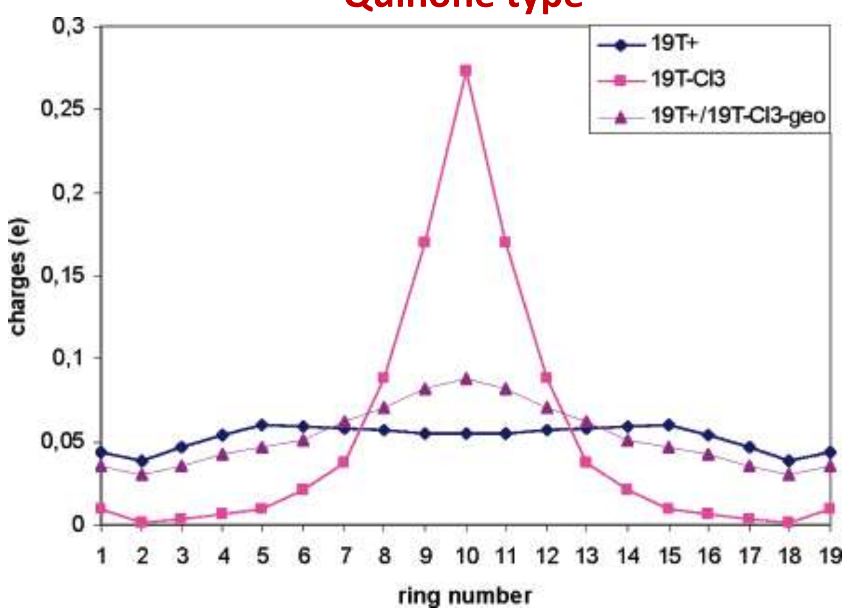


Charge storage in polythiophene (PT)



Neutral polymer
Undoped

Cation radical
(Polaron)



U. Salzner, *J. Chem. Theory Comput.* **2007**, *3*, 1143

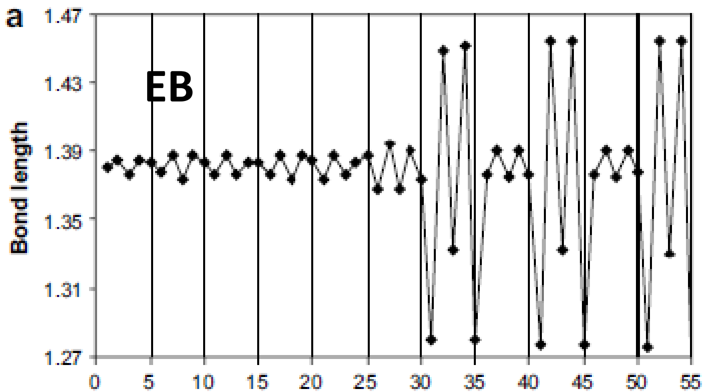
Polythiophene

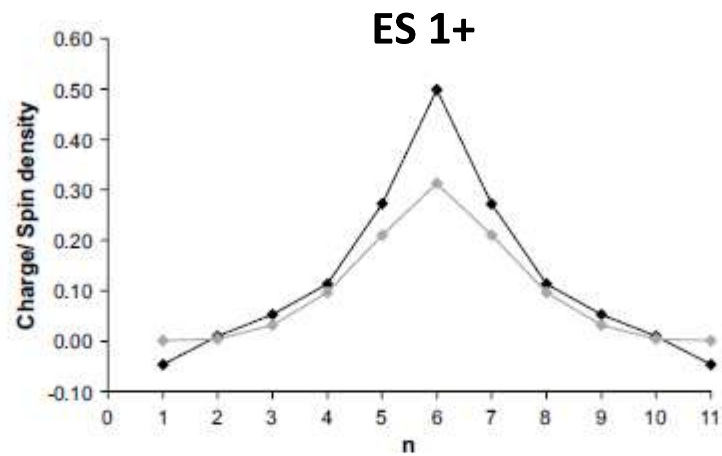
12T

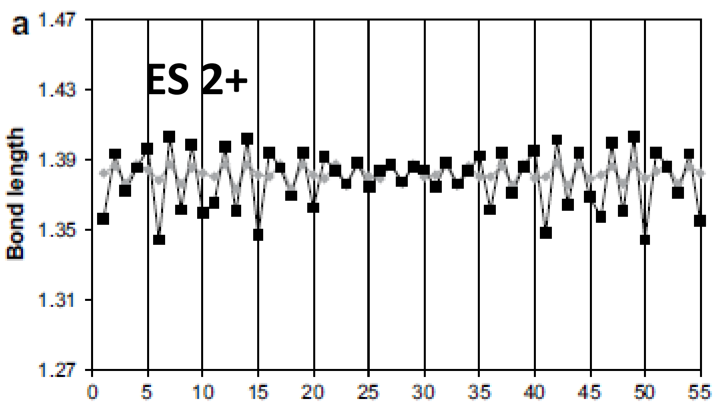
HOMO

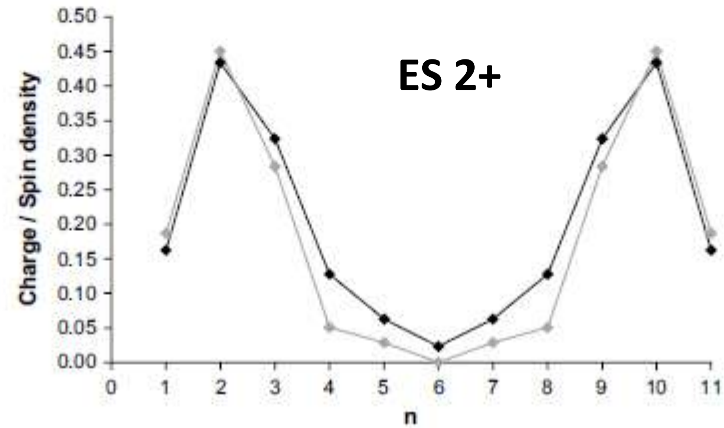
20T

Electronic structure of PANI

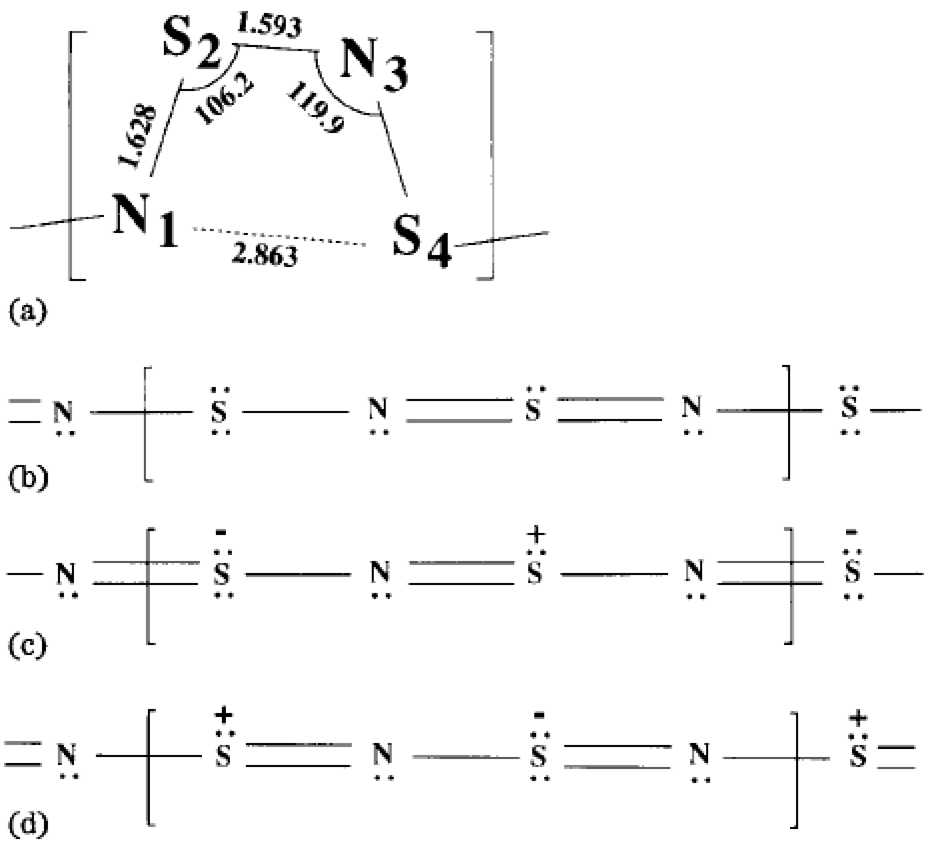


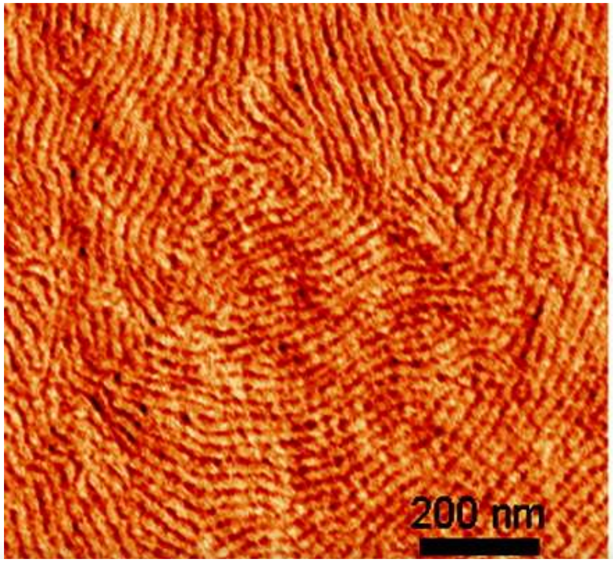


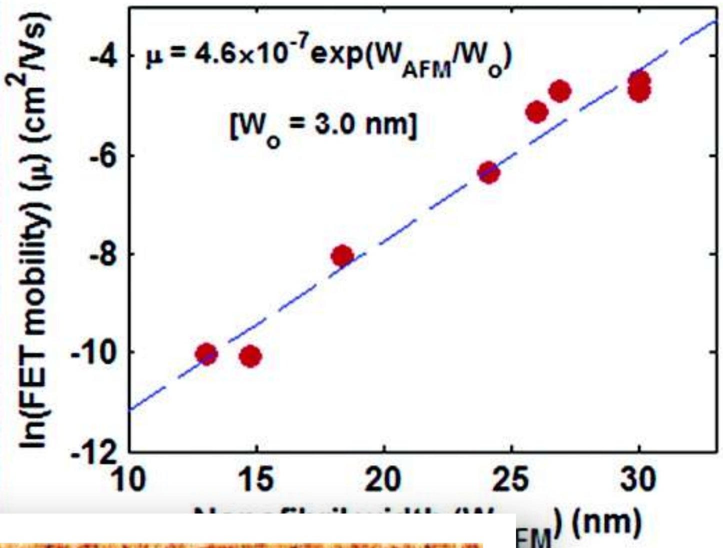


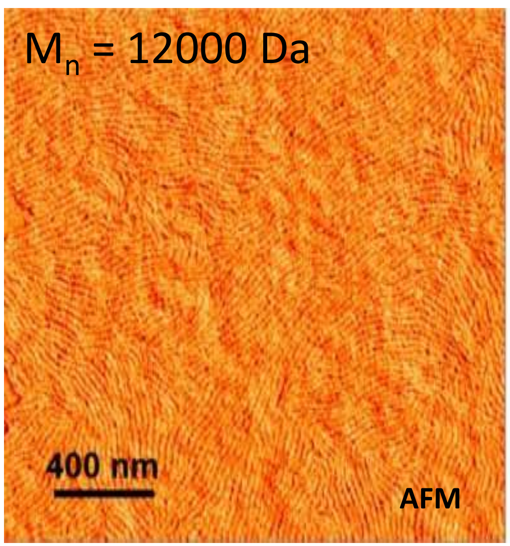


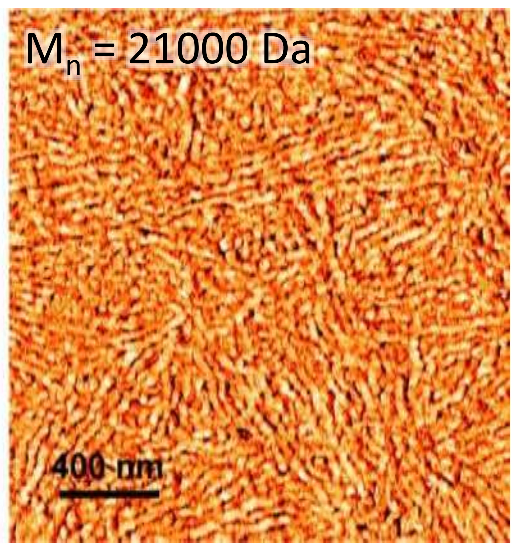
$(SN)_x$




200 nm


$\mu = 4.6\times10^{-7}\exp(W_{AFM}/W_o)$
$[W_o = 3.0\ nm]$
ln(FET mobility) (μ) (cm^2/Vs)
-4
-6
-8
-10
-12
10
15
20
25
30
) (nm)


M_n = 12000 Da
400 nm
AFM


M_n = 21000 Da
400 nm

Synthesis

- ***Chemical Synthesis***
- ***Electrochemical Synthesis***
- ***Photochemical***
- ***Biocatalyzed Synthesis***
- ***Solid-state***