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Semiconducting Polymers:
Synthesis and properties

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Polymer = macromolecule

Polymers:
Molecules with high molecular weight (**macromolecules**) composed of repeating structural units.
Synthesized from low molecular weight molecules (**monomers**) by means of a proper polymerization process.

Physical states:	solid state
	liquid state (with high viscosity)
	peculiar elastomeric state

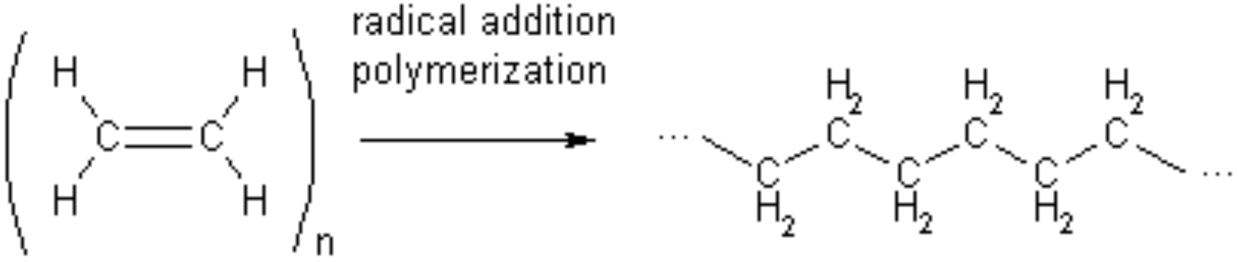
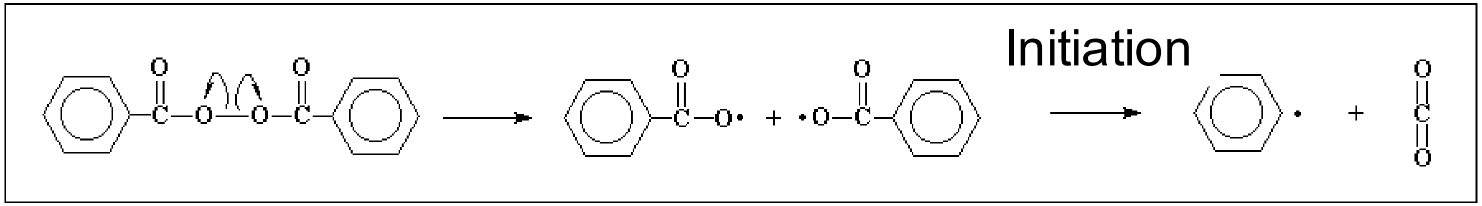


Fig 1: The polymerisation of ethene in to poly(ethene)

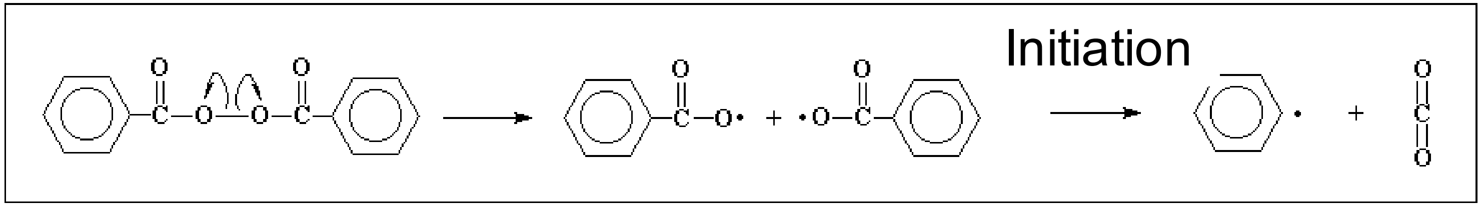
Polymerization process

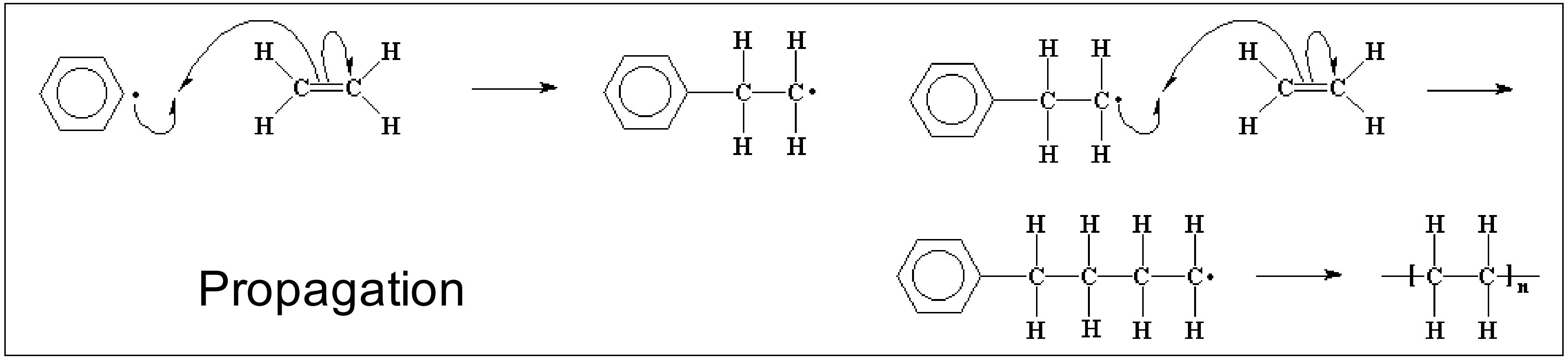
Example : radical polymerization (chain-growth polymerization)



Polymerization process

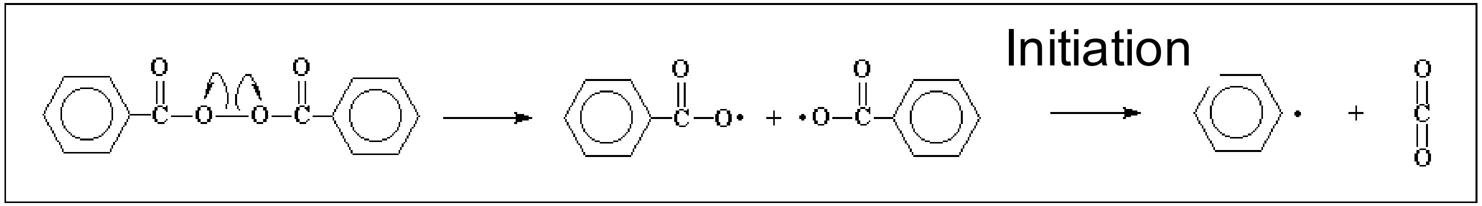
Example : radical polymerization (chain-growth polymerization)



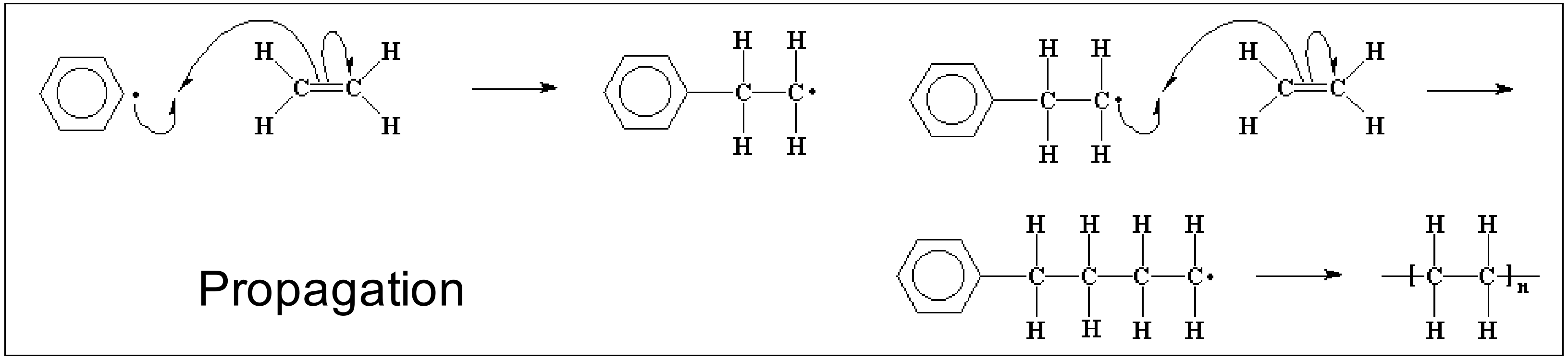


Polymerization process

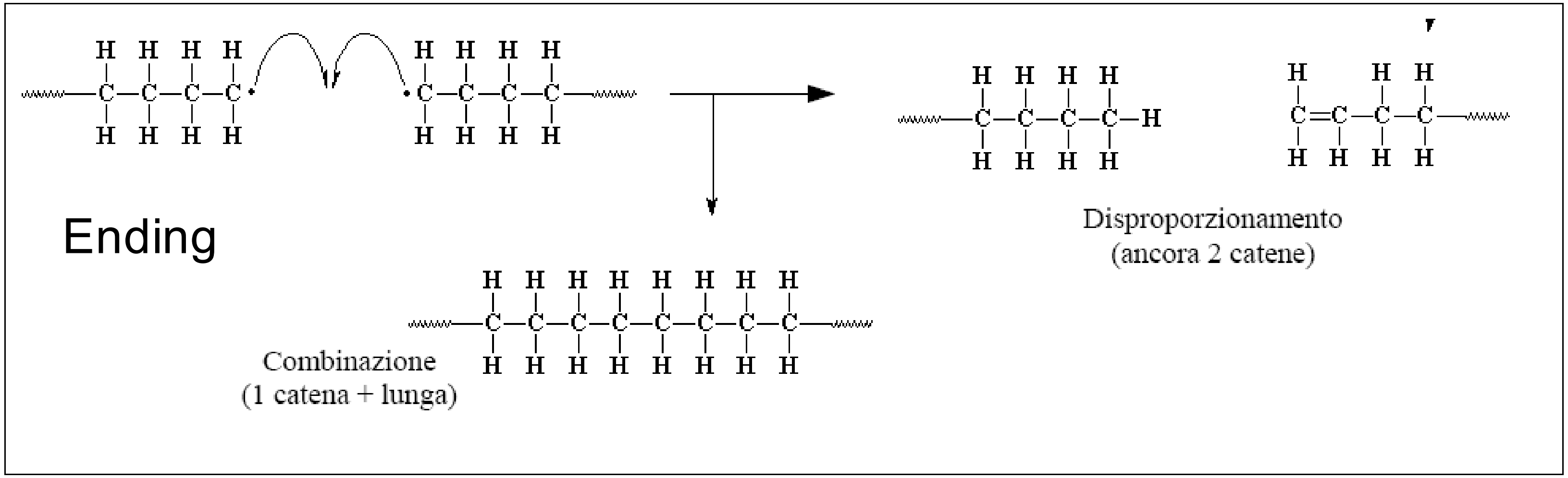
Example : radical polymerization (chain-growth polymerization)



Initiation



Propagation



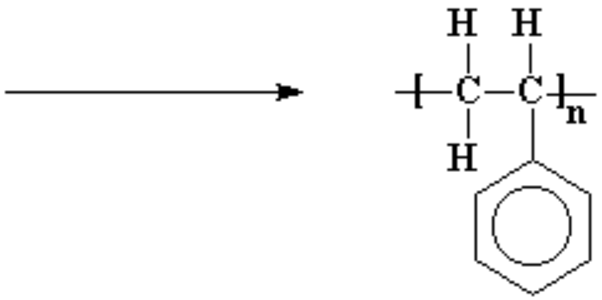
Ending

Disproporzionamento
(ancora 2 catene)

Combinazione
(1 catena + lunga)

Polymer materials

A **macromolecule** consists in elements linked together through strong bonds (covalent).



polystyrene

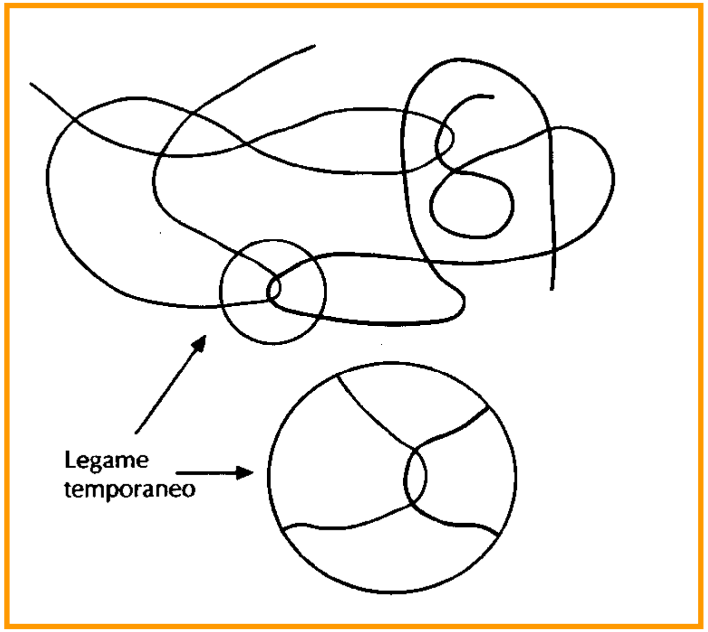
A **polymer** consists in a number of macromolecules interacting through weak bonds (i.e Van der Waals, hydrogen bonding).

Macromolecules are interpenetrating and accordingly:

✓Limited molecular mobility (translational)

✓(physical) entanglements = temporary physical bond, which can break and restore under suitable conditions.

✓ weak bonds between chains implies that they chains can slide (material deformation)

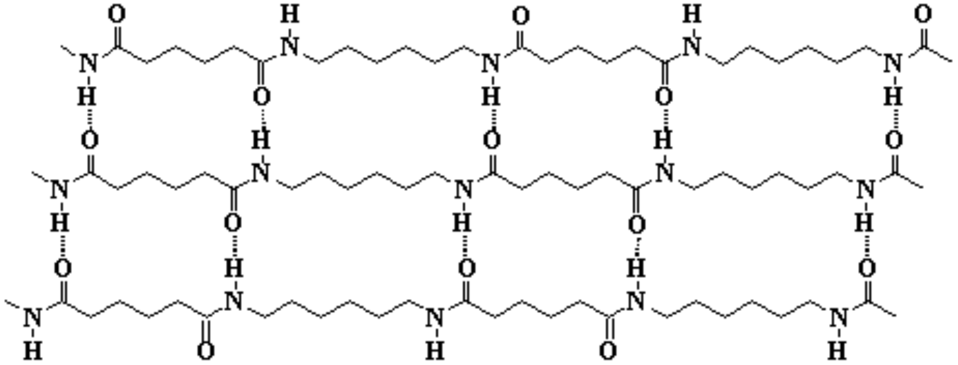


Chemical structure of monomeric units

A **polymer** consists in a number of macromolecules interacting through weak bonds (i.e Van der Waals, hydrogen bonding).

$$\left[CH_2 - CH_2 \right]_n$$

$T_m = 135°\ C$

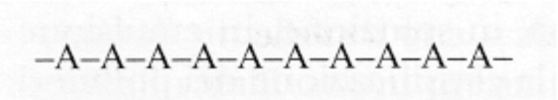


In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

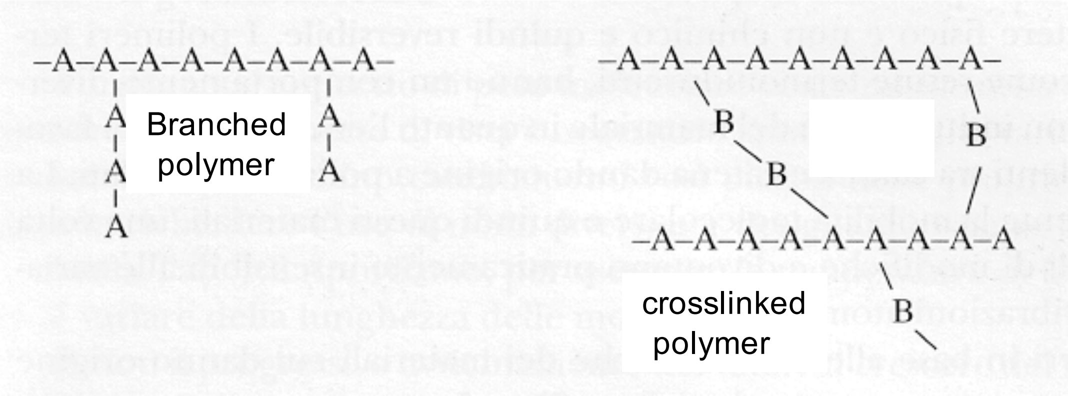
Polar groups
Stronger intermolecular interactions

$T_m \sim 200°\ C$

Polymer chain structure



Linear polymer



Linear polymers: thermoplastic

Branching: with the same average molecular weight, branched polymers are more soluble, less resistant to chemicals and environment; viscosity decreases due to the less effective entanglements.

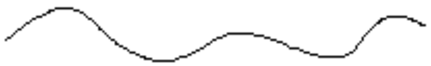
Cross-linking: molecular long range mobility is reduced.
Properties depends on the degree of crosslinking.
Not soluble
Cross-linked polymers can not be melted.

Polymer chain structure

Branching– example: **polyethylene**

$$\left[CH_2-CH_2 \right]_n$$

linear



HDPE
Well effective intermolecular packing
Higher density
Higher crystallinity

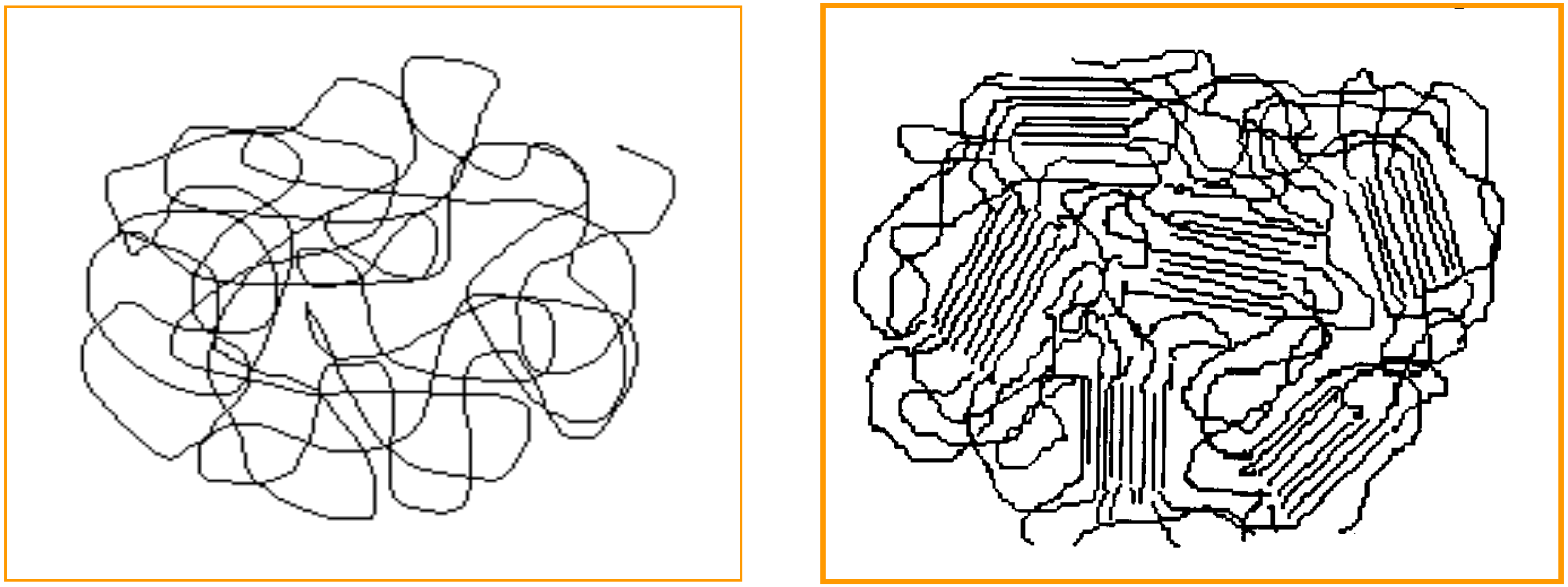
$T_m \sim 135^\circ C$

branched

LDPE
Less effective packing
Lower density
Lower crystallinity

$T_m \sim 110^\circ C$

Amorphous polymers vs crystalline polymers



To promote crystallization:
Chain regularity
Long-range order

Crystalline vs amorphous:
higher density(10-15%)
Higher stiffness
Resistance to solvents, chemicals, acids/bases.

Crystallinity: molecular requirements

homopolymer

–A–A–A–A–A–A–A–A–A–A–

Linear polymer

LLDPE: Melting Temp. Range 120 to 160 ° C

Co-polymers: polymers consisting in more than one monomeric unit (i.e A and B)

—A—B—A—B—A—B—A—B—A—B—A—B—A—B—

alternating copolymer

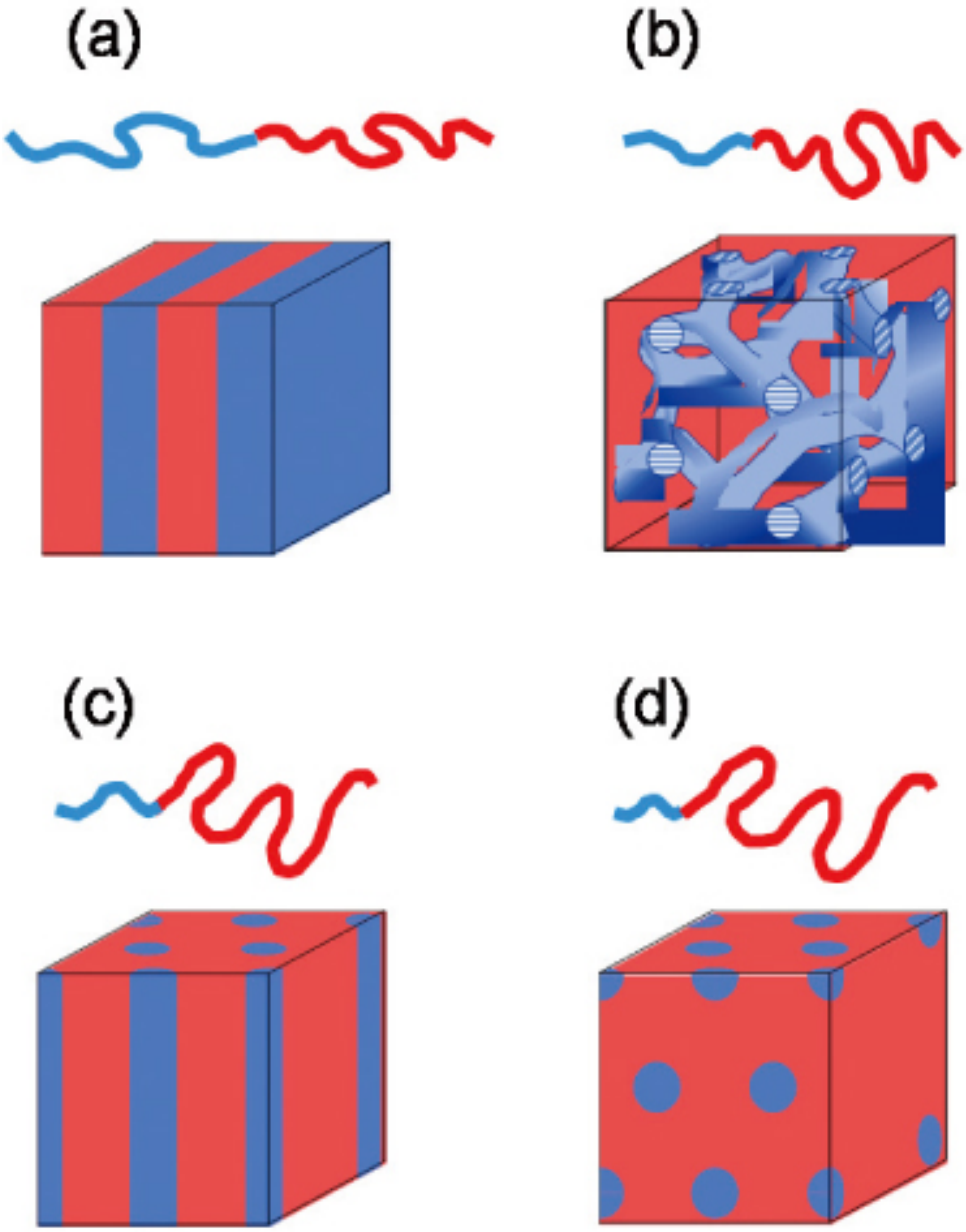
—A—A—B—A—B—B—A—B—A—A—B—B—B—A—

random copolymer

—A—A—A—A—A—A—A—B—B—B—B—B—B—B—

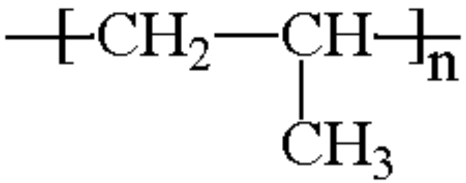
block copolymer

Block copolymers

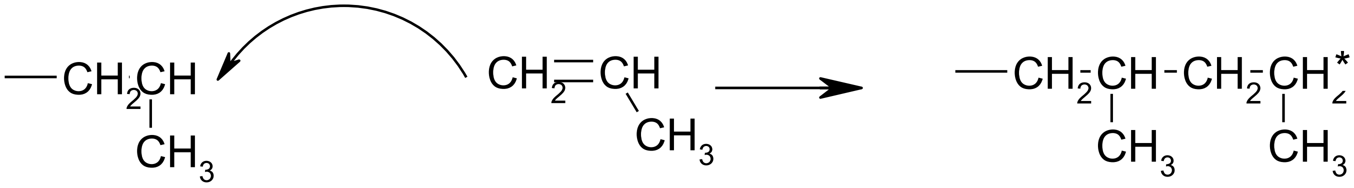


Crystallinity: regio-regularity

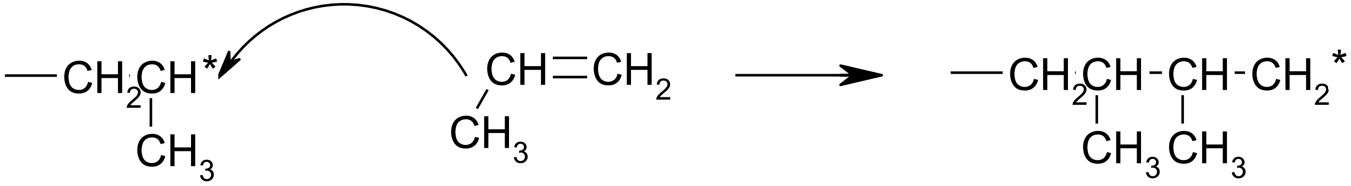
example: **polypropylene**



$$\left[CH_2 - \underset{\displaystyle CH_3}{CH} \right]_n$$



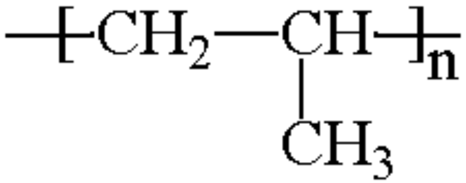
head to tail insertion → REGIOREGULAR polymer



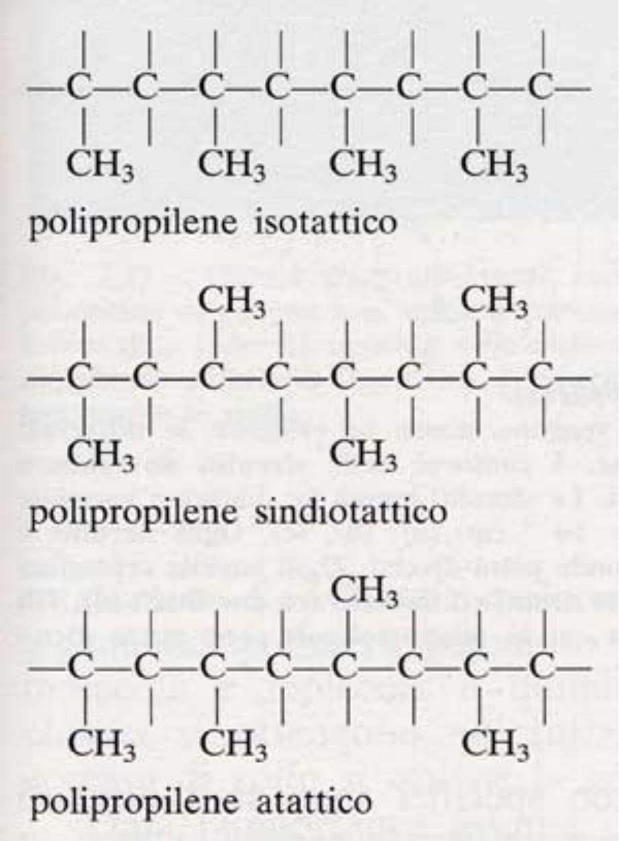
inversions
(head to head, tail to tail) → REGIORANDOM polymer

Crystallinity: tacticity (position of lateral groups)

Example: **polypropylene**



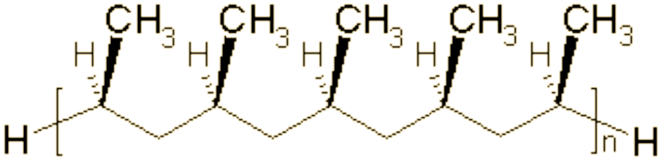
$$-\!\left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right]_n\!-$$



polipropilene isotattico

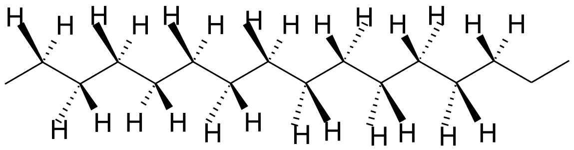
polipropilene sindiotattico

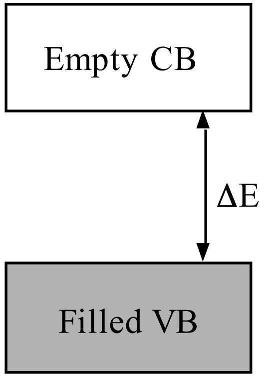
polipropilene atattico



Conjugated polymers: structure and properties

$-(CH_2-CH_2)n-$

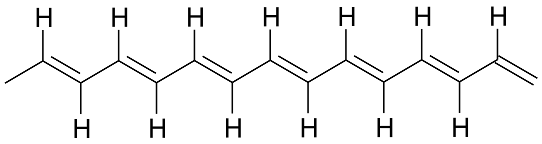


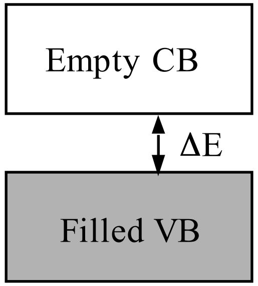


- ✓ σ Bond

- ✓ insulator
- ✓ solubility

$-(CH=CH)n-$



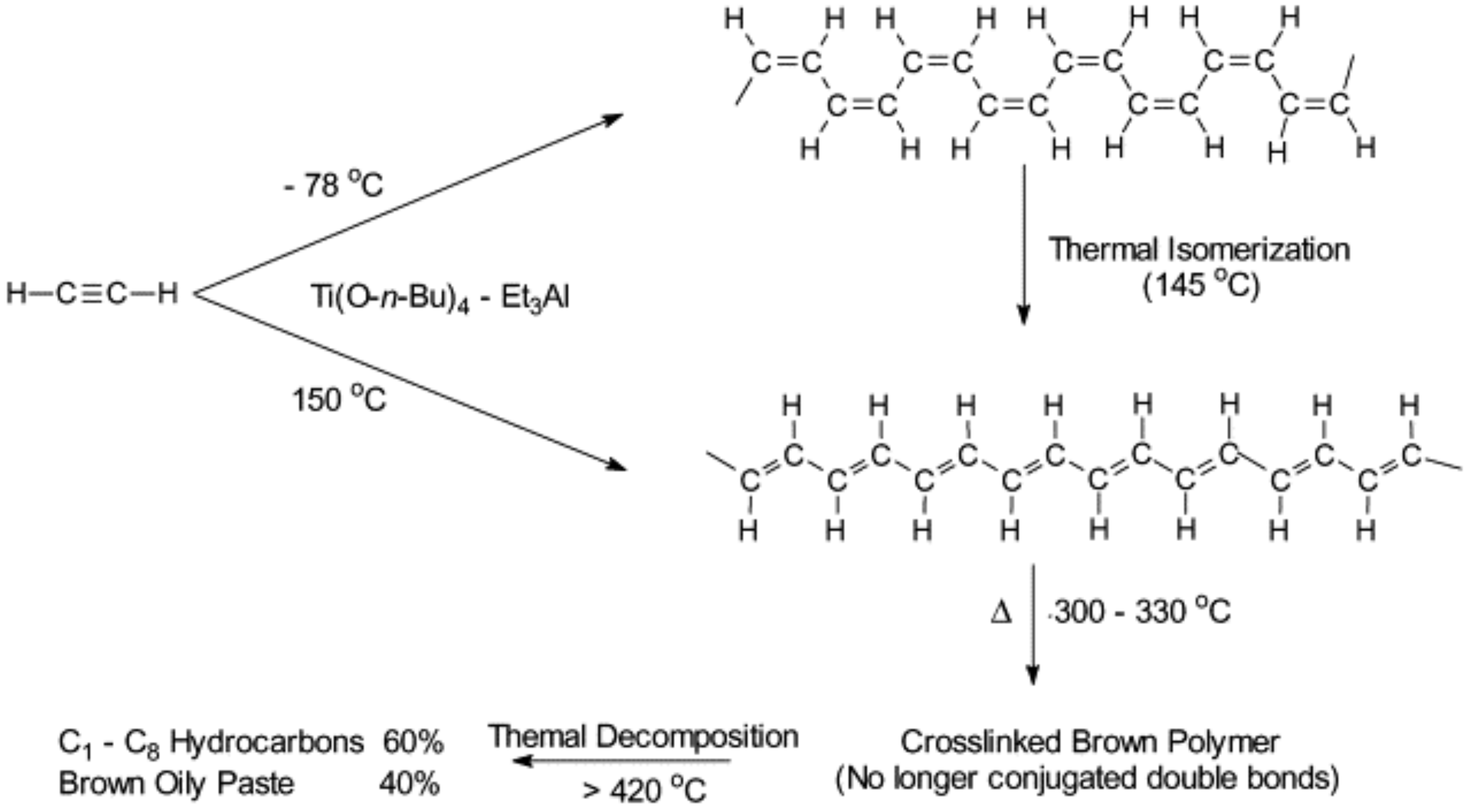


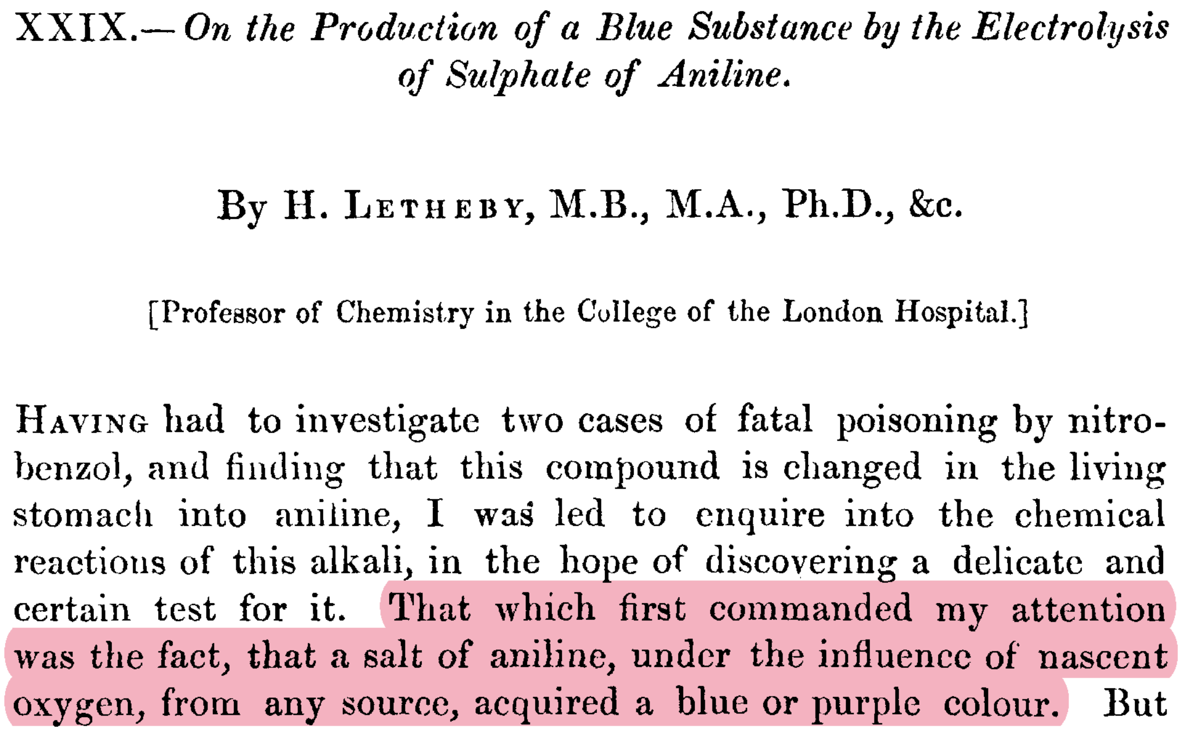
- ✓ Delocalized π bonds

- ✓ more rigid chain
- ✓ less entanglements
- ✓semiconductors

1st synthesis of a “conducting polymers”

G. Natta, G. Mazzanti and P. Corradini, *Atti Acad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat., Rend.*, (8), 25: 3 (1958)





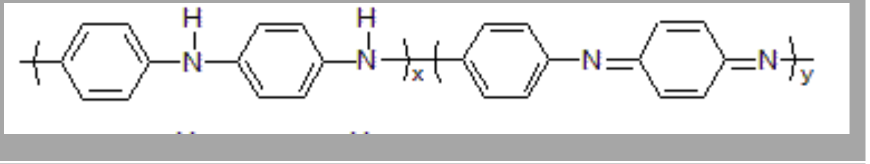
XXIX.—*On the Production of a Blue Substance by the Electrolysis of Sulphate of Aniline.*

By H. Letheby, M.B., M.A., Ph.D., &c.

[Professor of Chemistry in the College of the London Hospital.]

Having had to investigate two cases of fatal poisoning by nitrobenzol, and finding that this compound is changed in the living stomach into aniline, I was led to enquire into the chemical reactions of this alkali, in the hope of discovering a delicate and certain test for it. That which first commanded my attention was the fact, that a salt of aniline, under the influence of nascent oxygen, from any source, acquired a blue or purple colour. But

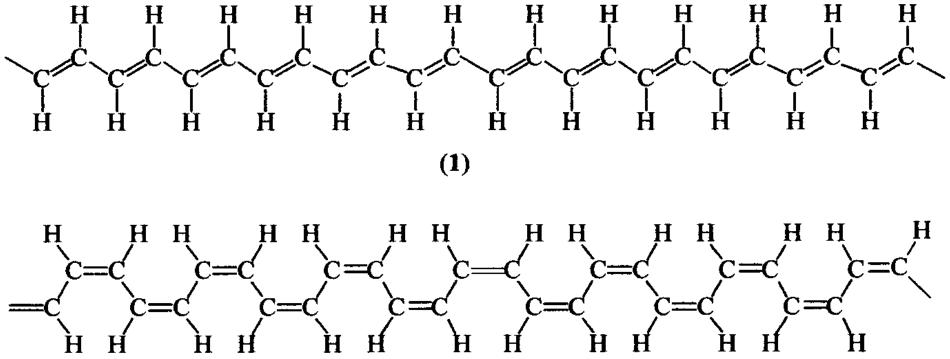
Letheby 1862: Polyaniline



1st synthesis of a conducting polymer

A.G. MacDiarmid

Shirakawa, Ikeda:1967-1974



(1)

(2)

Scheme 1. All-*trans* (1) and all-*cis* (2) polyacetylene.

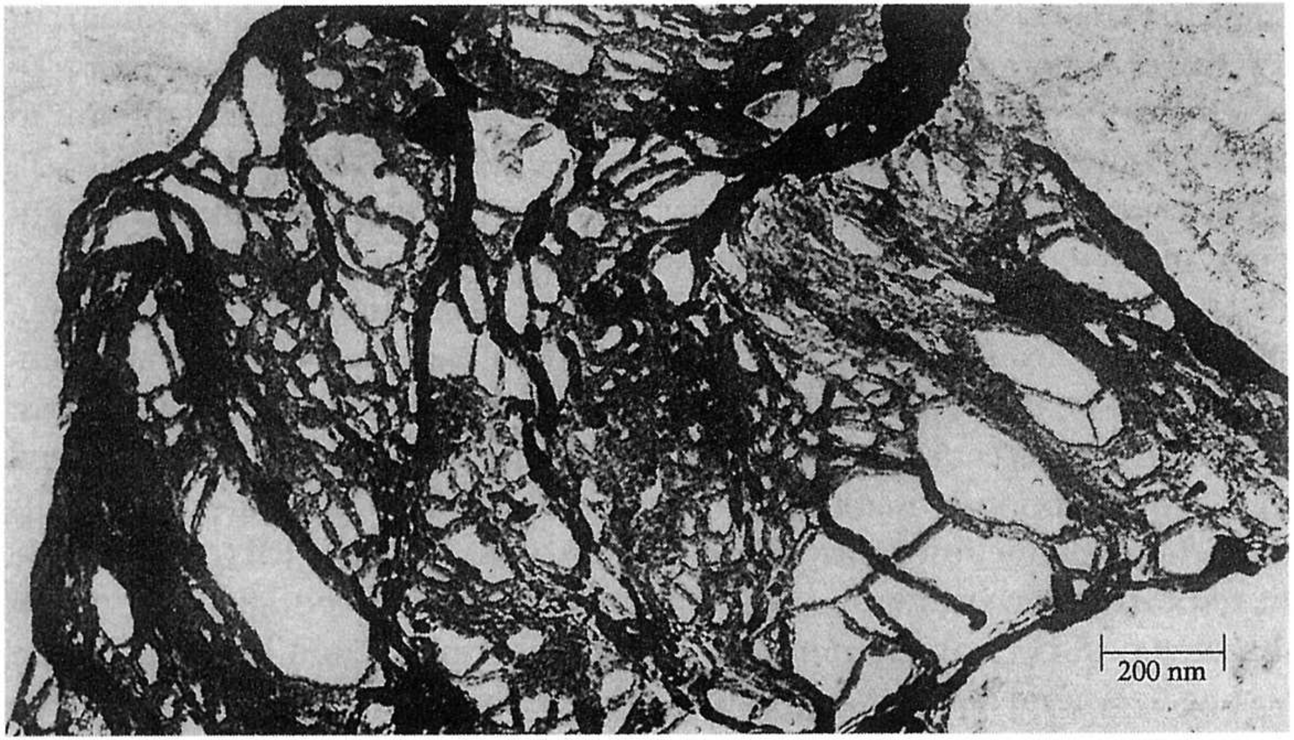


Figure 1a. Transmission electron micrograph of an extremely thin film of polyacetylene.

H. Shirakawa

Doping : effect on conductivity

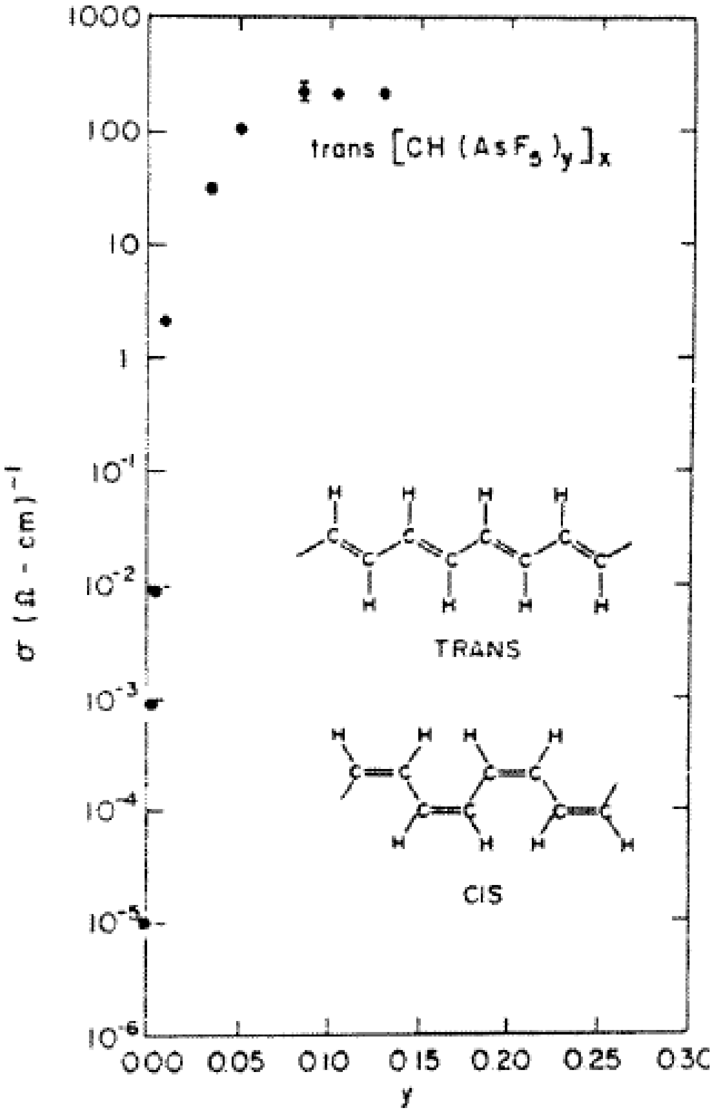
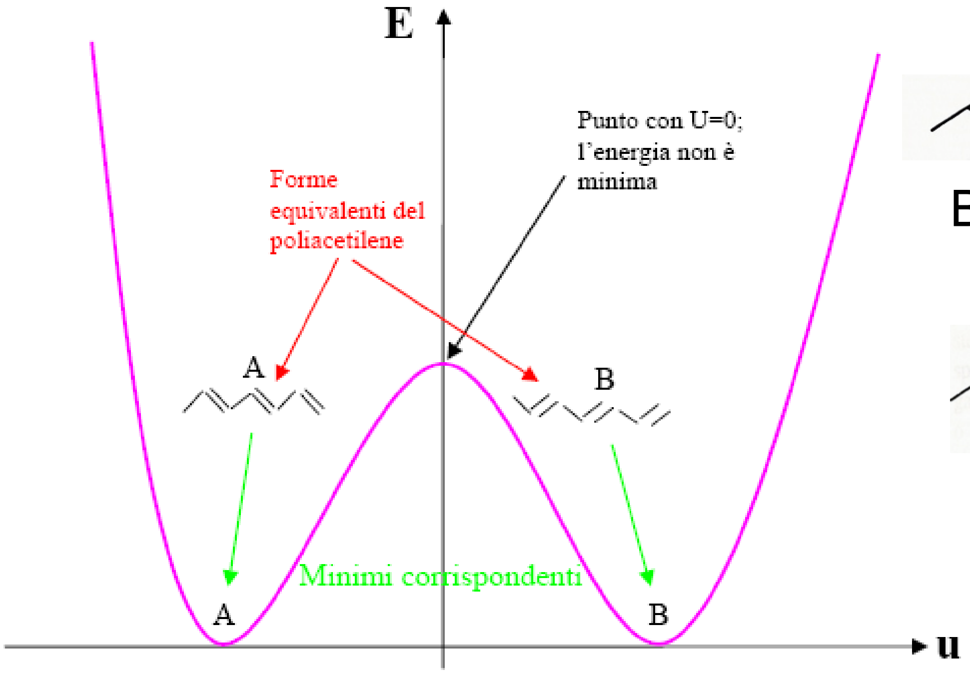
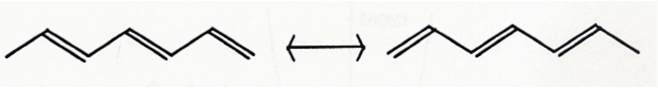


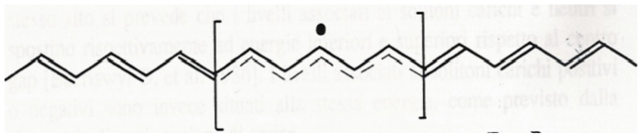
Figure 2. Electrical conductivty of *trans*-$(CH)_x$ as a function of (AsF_5) dopant concentration. The *trans* and *cis* polymer structures are shown in the inset.

Polyacetylene

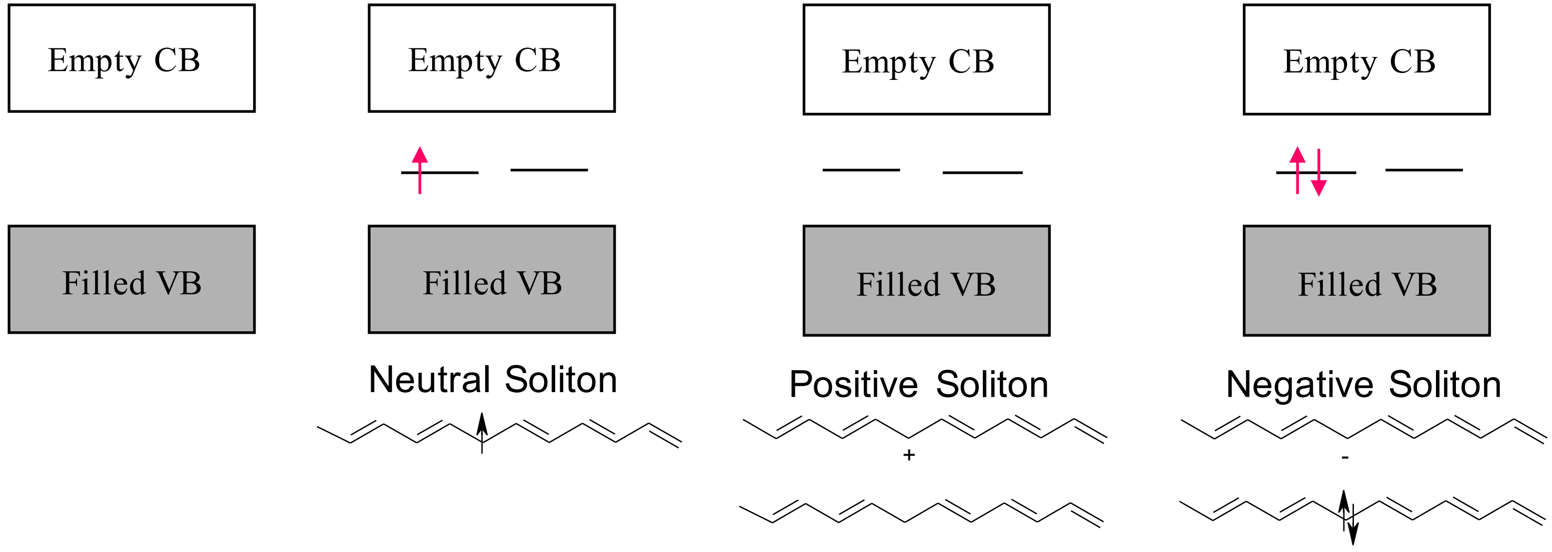




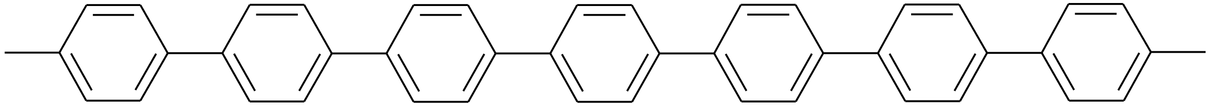
BLA = 0.1 Å



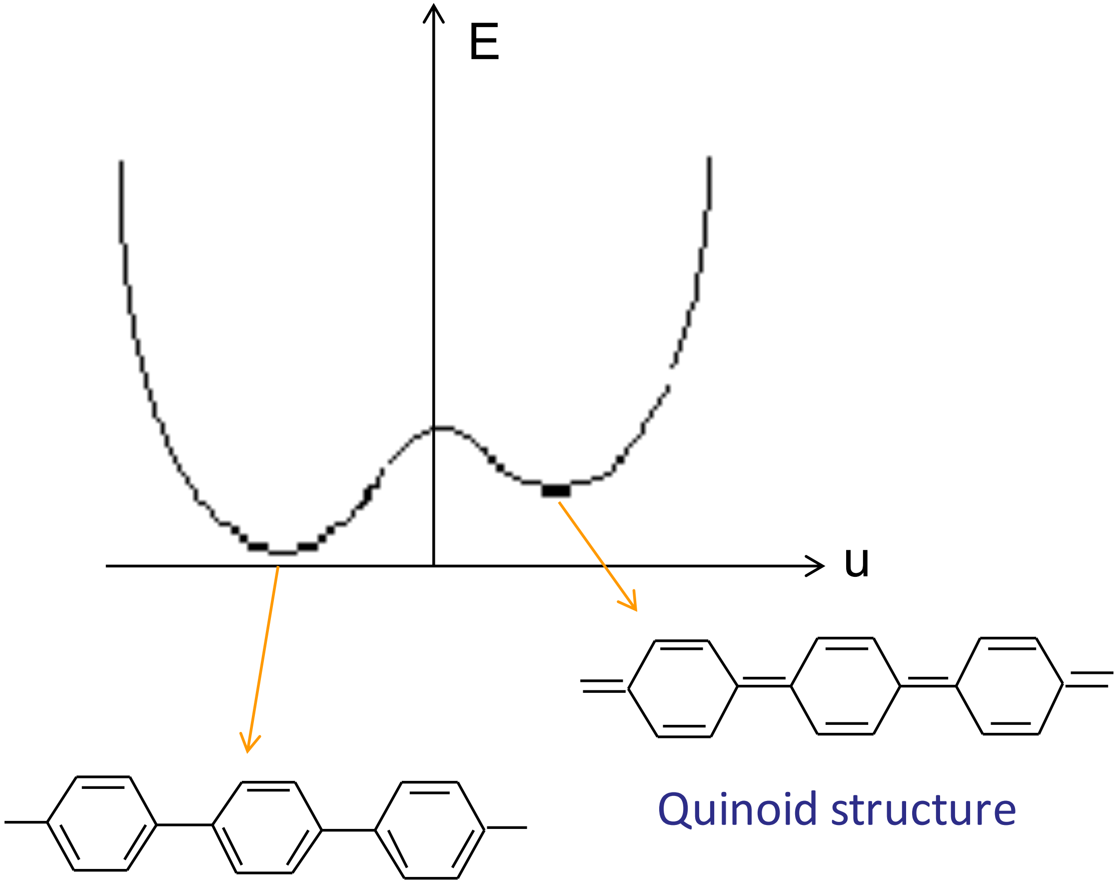
Neutral soliton



The other conjugated polymers



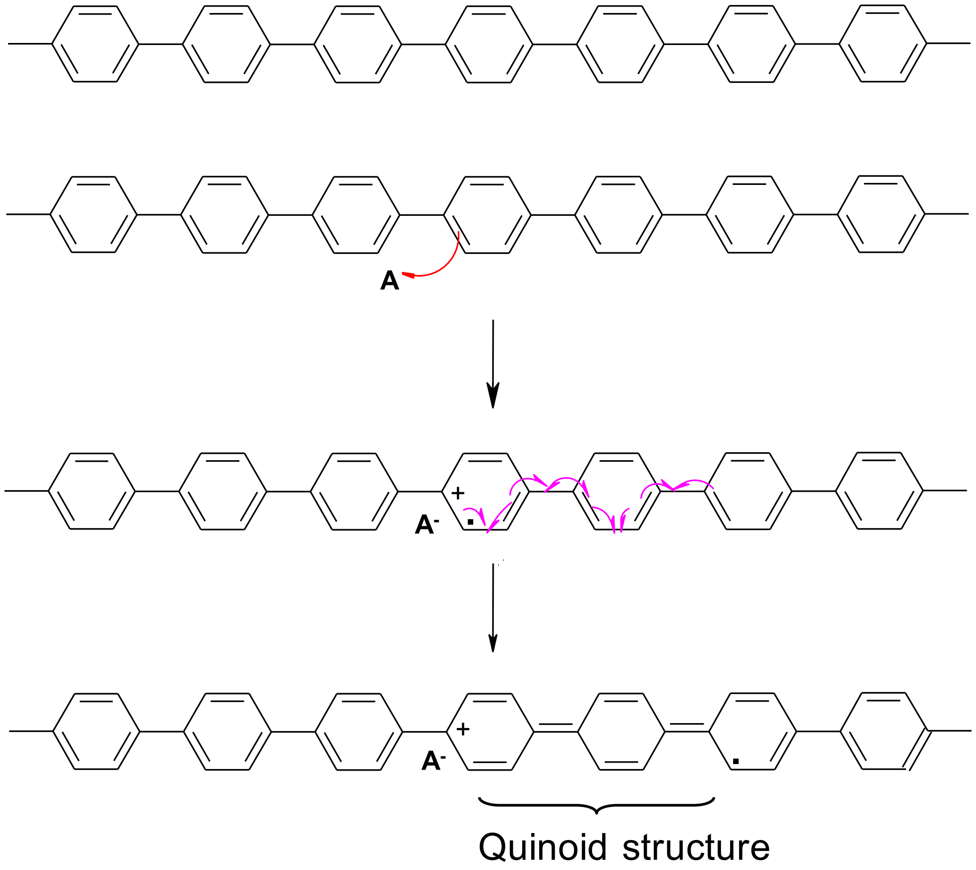
PPP



Quinoid structure

Aromatic structure

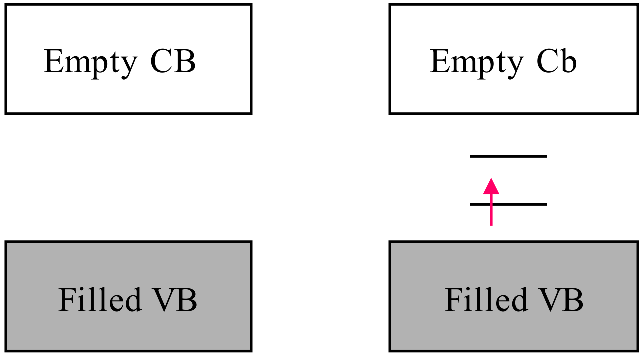
Doping: polarons



PPP

A = acceptor
= oxidizing species

A^- = dopant



Empty CB

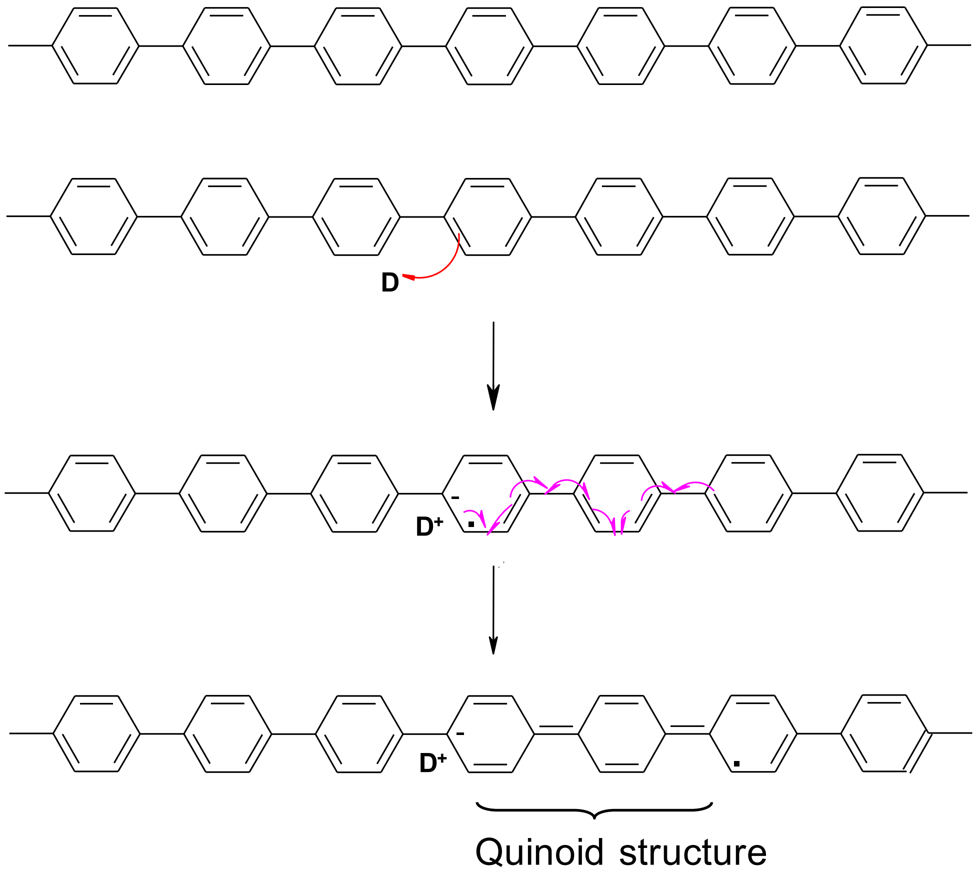
Empty Cb

Filled VB

Filled VB

p-doping

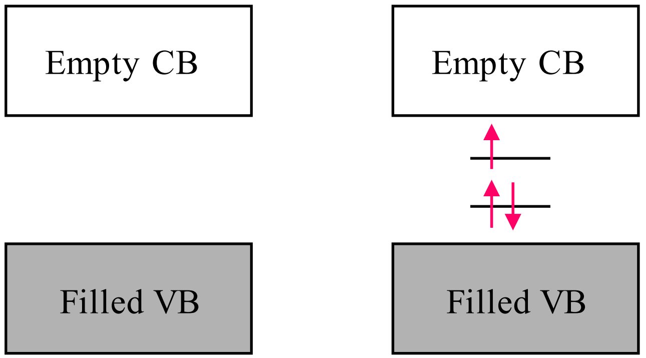
Doping: polarons



PPP

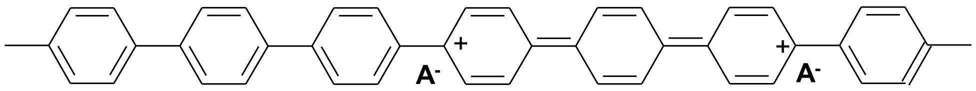
D = donor
= reducing species

D^+ = dopant

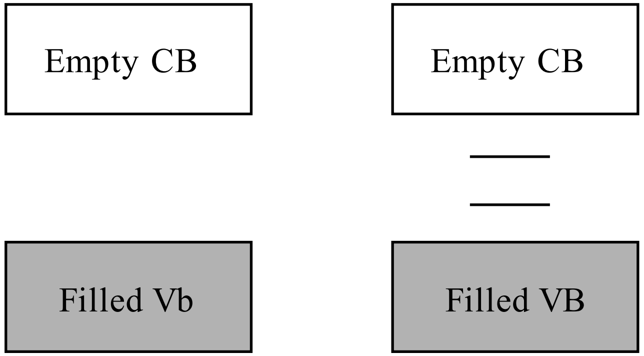


n-doping

Doping: bipolarons



p-doping

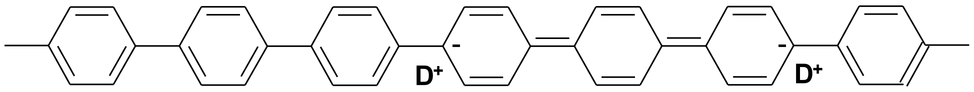


Empty CB

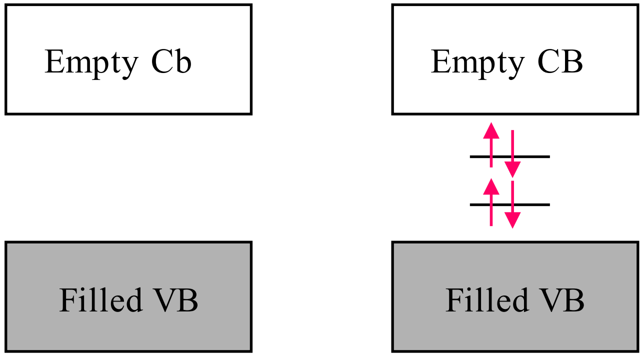
Empty CB

Filled Vb

Filled VB



n-doping

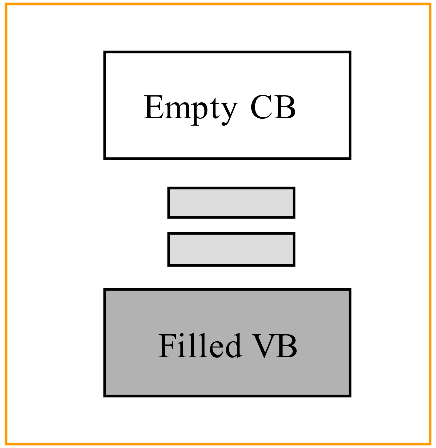


Empty Cb

Empty CB

Filled VB

Filled VB



Empty CB

Filled VB

Spinless conduction

Doping : effect on conductivity

Conductivity increases with increased doping

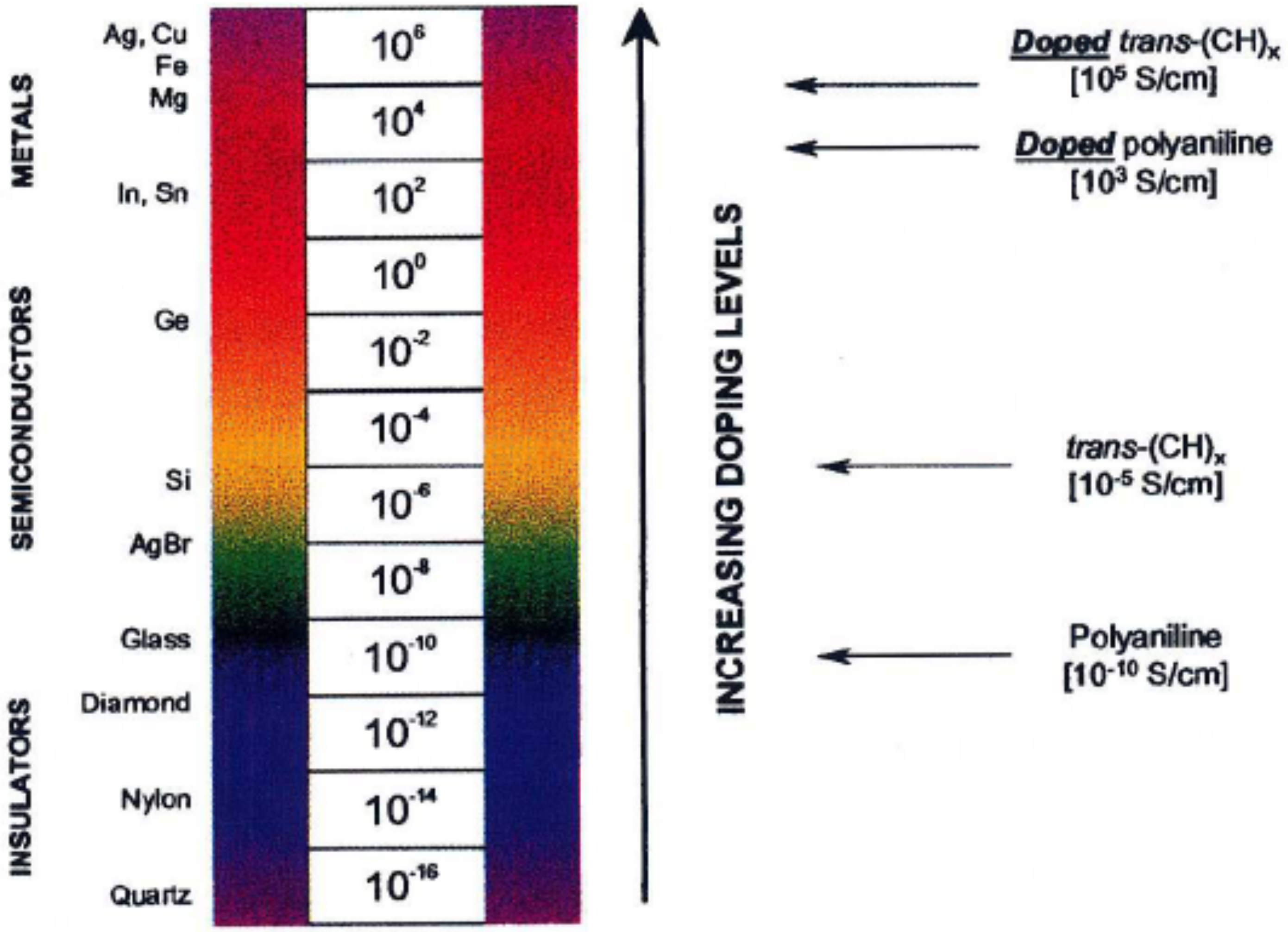
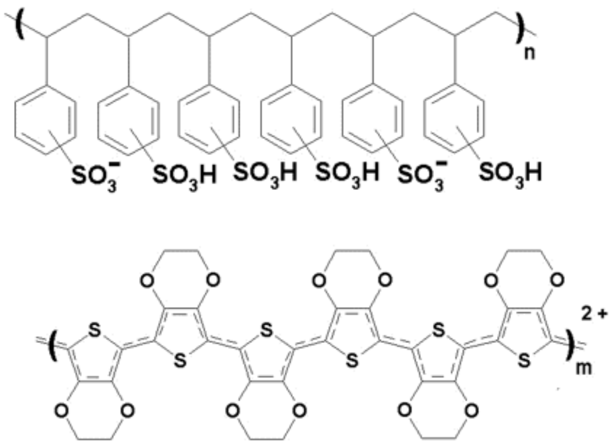
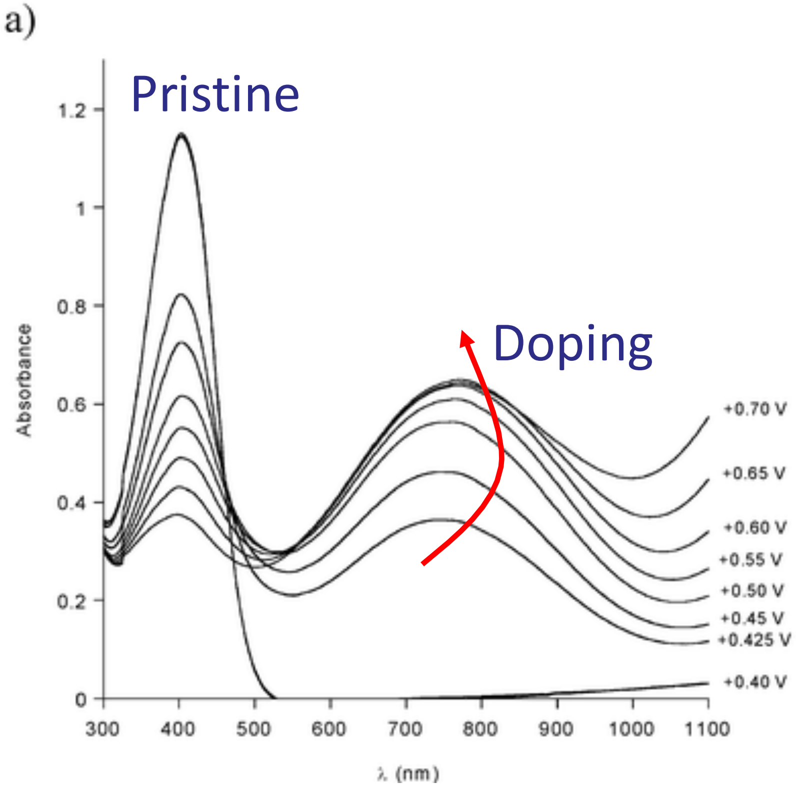


Figure 1. Conductivity of Electronic Polymers

Doping : effect on optical properties

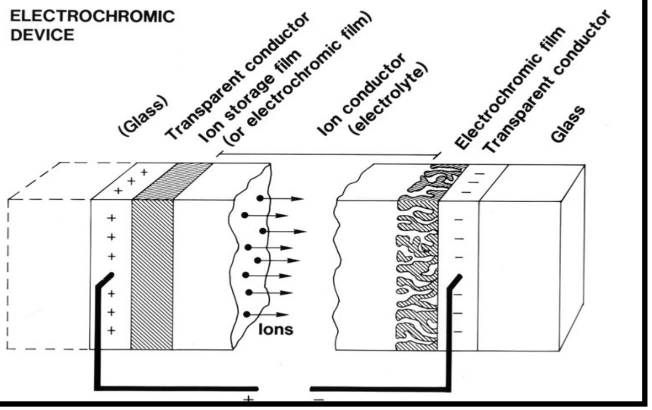
Baytron



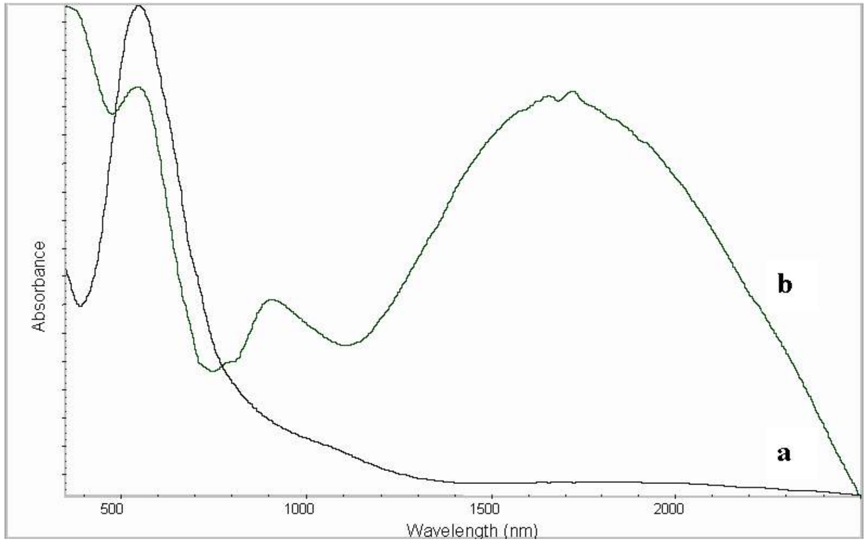


5 layers on transparent substrate:

- 2 electrodes
- Ion storage
- Electrolyte
- Electrochromic layer

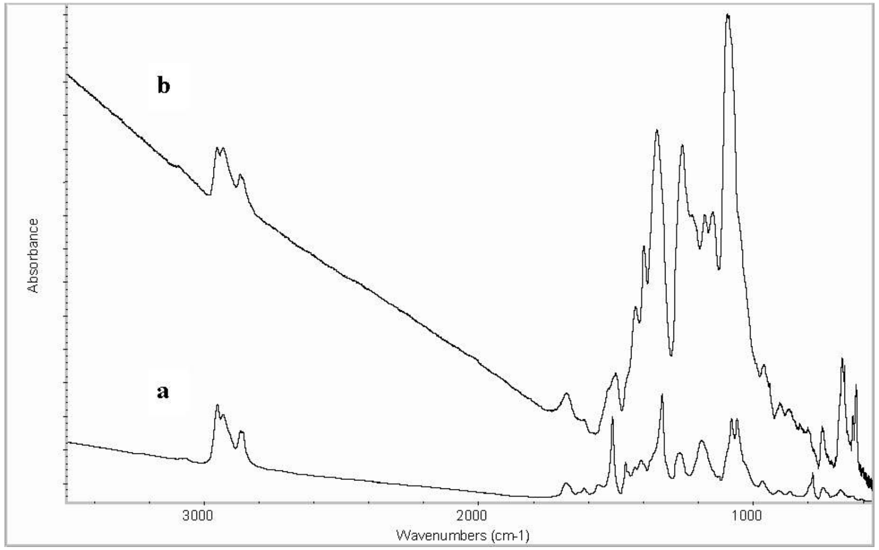


Doping : effect on optical properties



UV-vis range: chromic effect

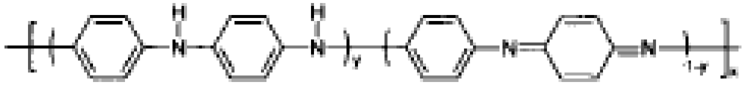
IR range: thermal comfort

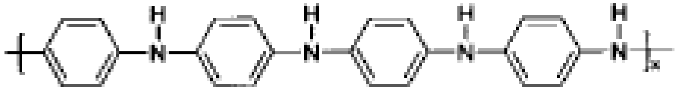


This photo and the next demonstrate the glare-reducing capabilities of SageGlass windows (installed in a test facility at Lawrence Berkeley National Laboratory).

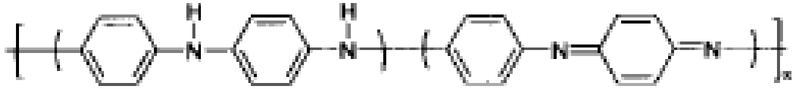
SageGlass®
The power to change™

Polyaniline: non redox doping

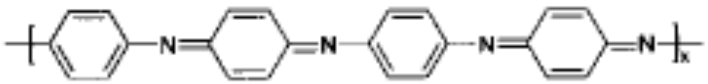




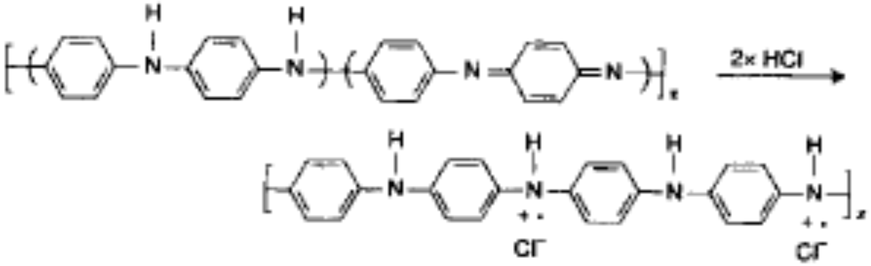
leucoemeraldine



emeraldine



pernigraniline



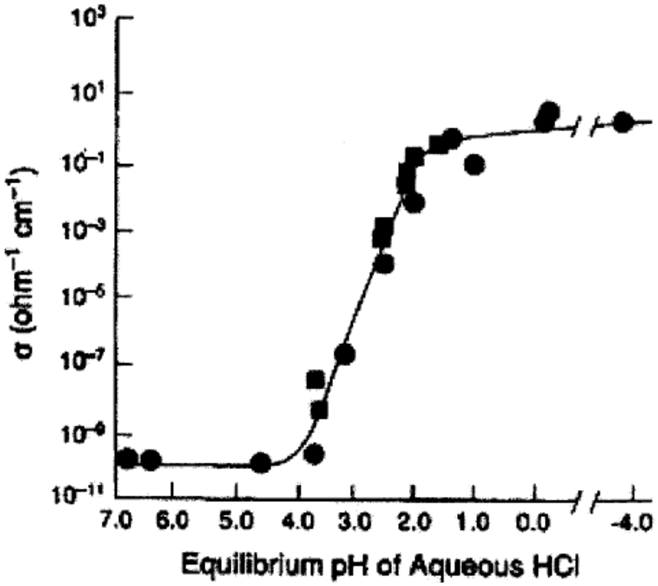
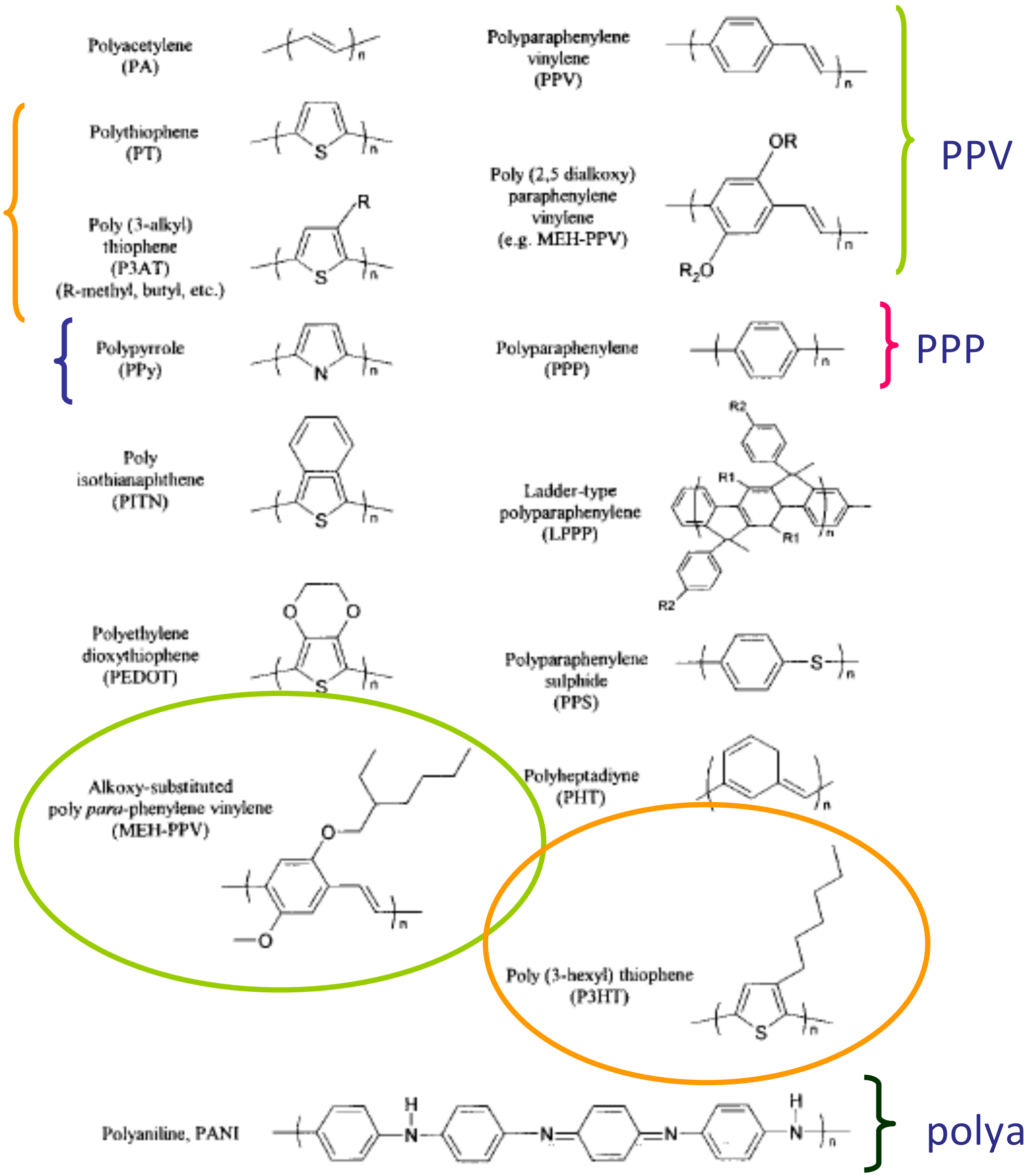


Figure 2. Conductivity of emeraldine base as a function of pH of HCl dopant solution as it undergoes protonic acid doping (● and ■ represent two independent series of experiments)[14,15].

Conjugated polymers



polythiophene

polypyrrole

PPV

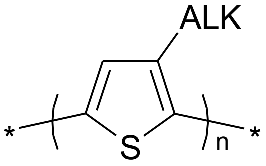
PPP

polyaniline (PANI)

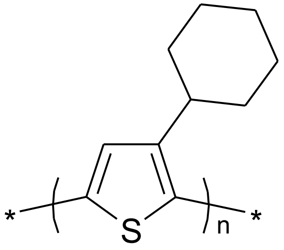
Figure 1. Molecular structures of a few conjugated polymers; note the bond-alternated structures.

Conjugated polymers

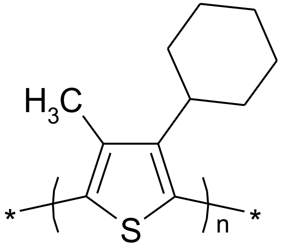
Effect of substitution: steric hindrance; electronic effect; solubility



red



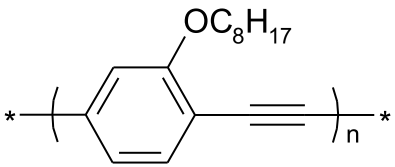
green



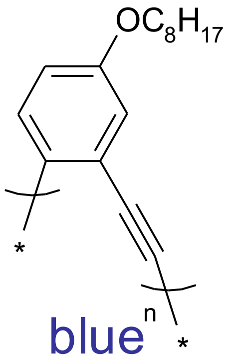
blue

Gil R.E., Malliaras G.G., Wildeman J., Hadziaonnou G. Adv. Mater. 1994, 6, 132
Kraft A., Grimsdale A.G., Holmes A.B., Angew. Chem. Int. Ed., 1998, 37, 402

Linking position:



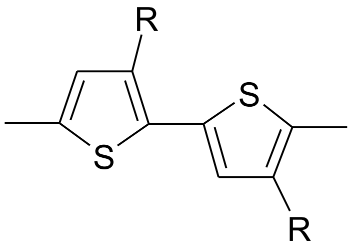
yellow

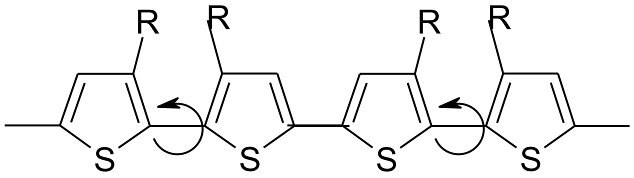


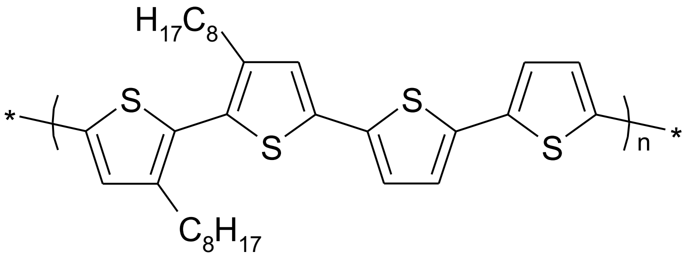
blue

Bunz U.H.F., Chem. Rev, 2000,100, 1605-1644

Chain distortion: effect on conjugation







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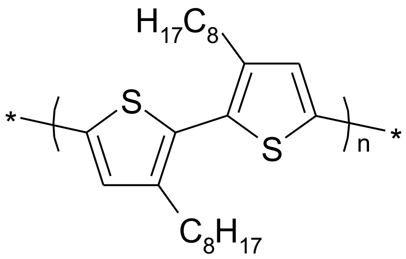

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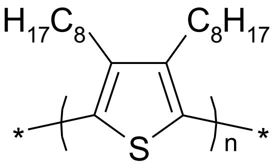
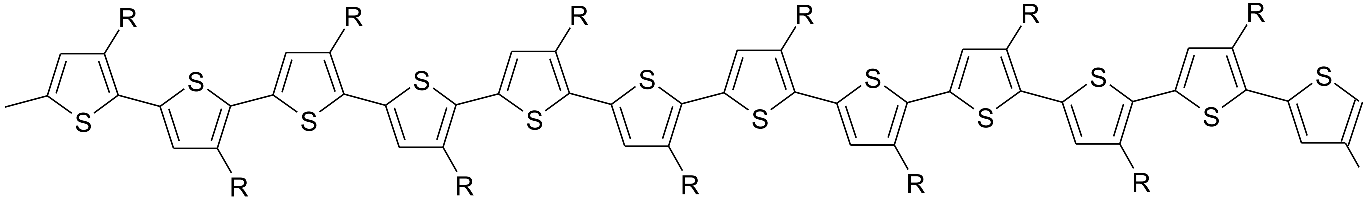
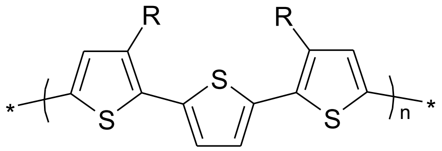


blue

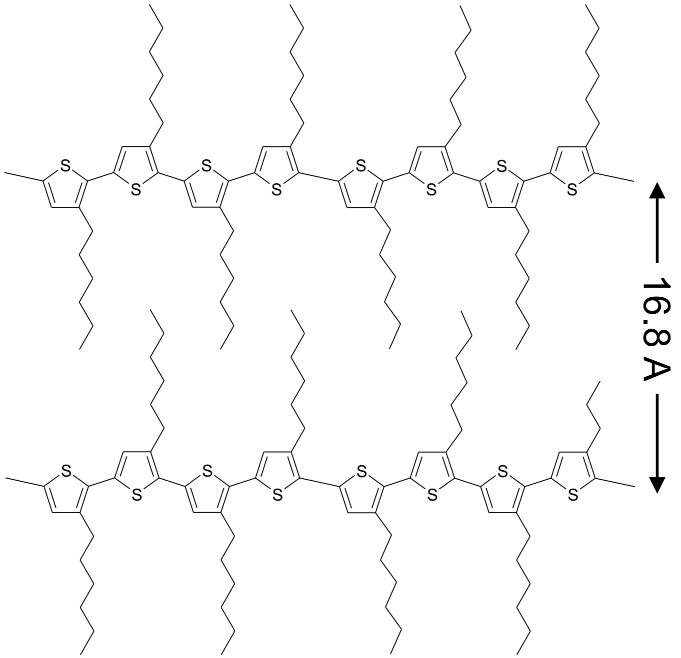
Regio-defined structures (P3HT)

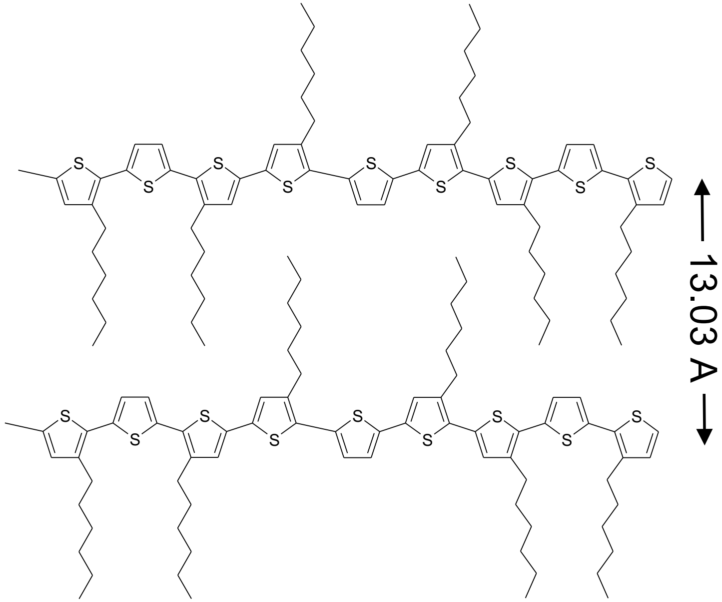


Mc Cullogh, Rieke



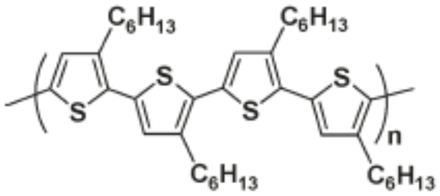
R = hexyl



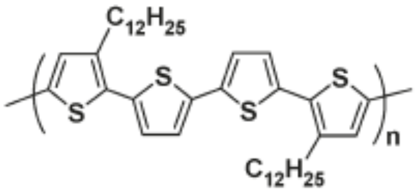


p-channel semiconductors

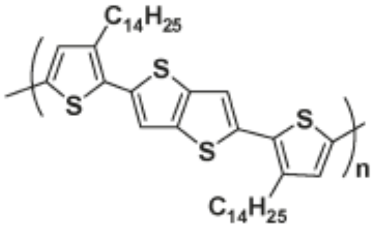
To date, the majority of the satisfactorily performing polymers for molecular electronics are p-channel.



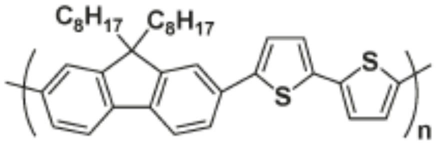
P3HT (P1)



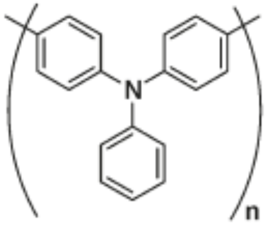
PQT-14 (P2)



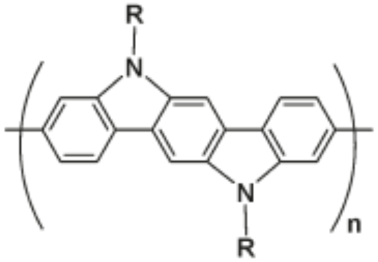
PBTTT-14 (P3)



F8T2 (P4)



PTAA (P5)



PCB-R (P6)

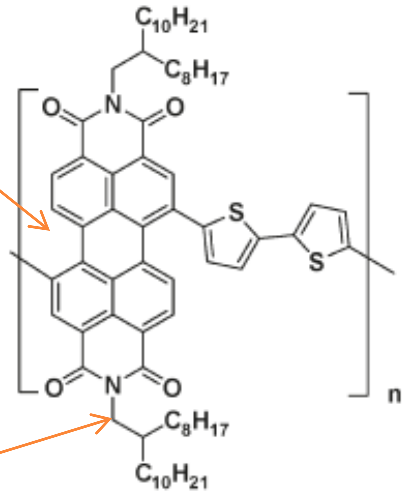
When E_{HOMO} is too high (low ionization potential), facile oxidation by air and acceptor sites dramatically compromise ambient stability.
For high ionization potential, devices typically suffer from unacceptably large threshold voltages.

n-channel semiconductors

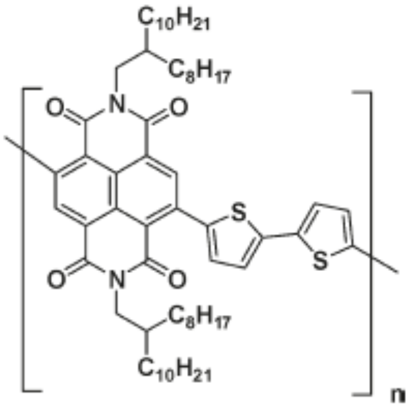
N-channel and, likewise, n-channel molecular systems have been traditionally underdeveloped compared to p-channel semiconductors.

ladder-type polymer exhibits high electron mobility of 0.1 cm2/(V s)

Solubilizing groups



P(PDI2OD-T2) (P57)



P(NDI2OD-T2) (P58)

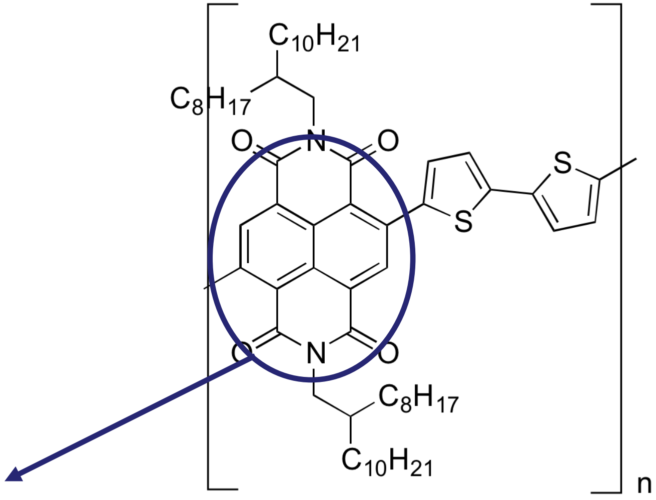
From an energetic perspective:

-a quite narrow energetic window for the LUMO level, located at about -4.0 ~ -4.3 eV, must be achieved to enable polymeric semiconductors with good charge transport in ambient.

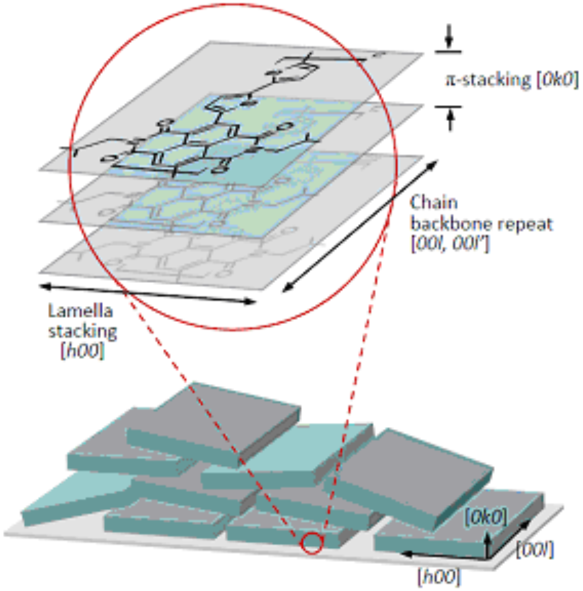
- For higher LUMO energy (low electron affinity), the polymer performance rapidly degrades after exposure to ambient atmosphere also when using electron-trap free dielectrics.

- for very low-lying LUMO systems (this has been well-established for molecular semiconductors), the corresponding devices are very difficult to turn-off.

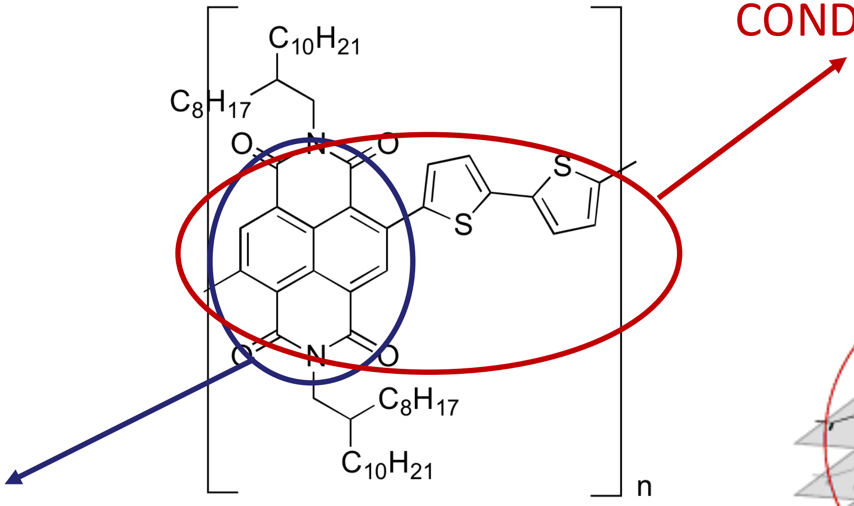
n-channel semiconductors



PLANARITY

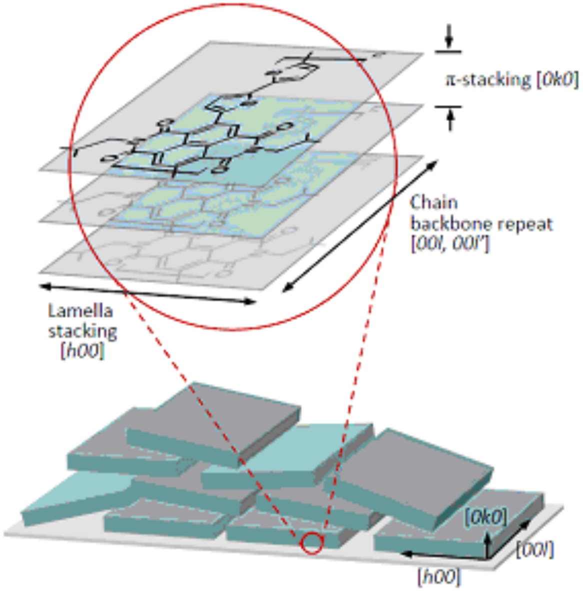


n-channel semiconductors

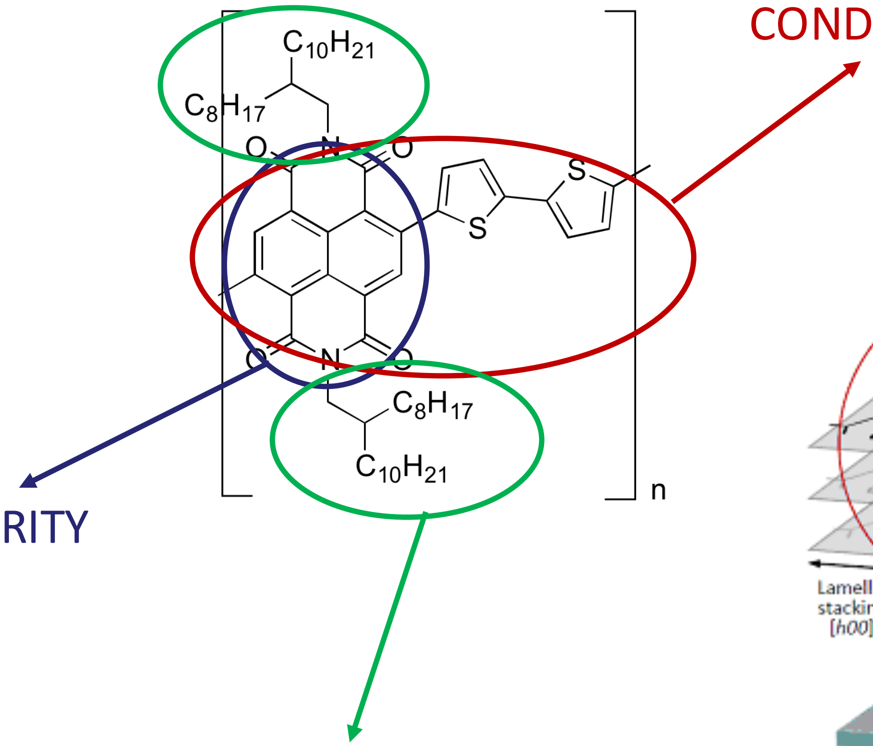


CONDUCTIVITY

PLANARITY



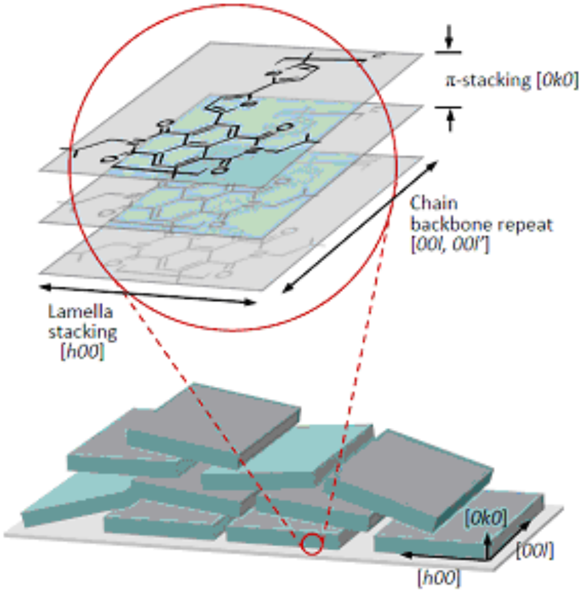
n-channel semiconductors



CONDUCTIVITY

PLANARITY

SOLUBILITY



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för upptäckten och utvecklan
av ledande polymerer
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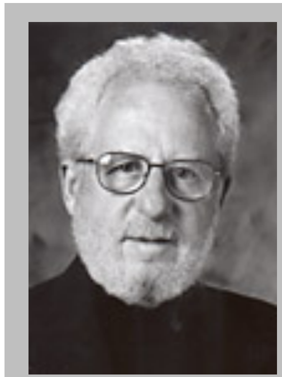

Heeger

McDiarmid

Shirakawa

We have been taught that plastics, unlike metals, do not conduct electricity. In fact plastic is used as insulation round the copper wires in ordinary electric cables. Yet this year's Nobel Laureates in Chemistry are being rewarded for their revolutionary discovery that plastic can, after certain modifications, be made electrically conductive….