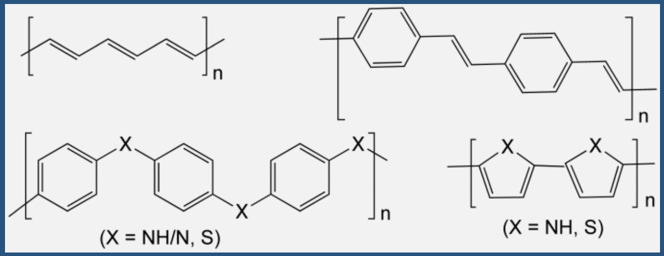
CHEM3020: POLYMER CHEMISTRY

Unit-5: Conducting Polymers



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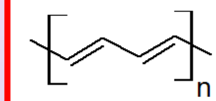
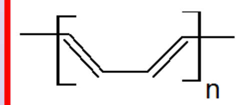
Conducting Polymers: polyacetylene, polyaniline

Usually, polymers insulate and do not conduct electricity and so electric wires are coated with polymers to protect them. Conducting polymers are usually polyconjugates (extended π- electron) structures, organic polymers which are insulators in the pure state but when treated with an oxidizing or a reducing agent can be converted into polymer salts with electrical conductivities comparable to metals.

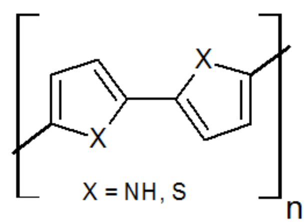


trans-Polyacetylene



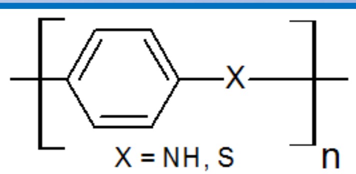
cis-Polyacetylene

Polyaniline was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that reduced form was colorless but the oxidized forms were deep blue.



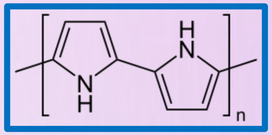
Polypyrrole (NH), Polythiophene (S)

Linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers are the main class of conductive polymers.

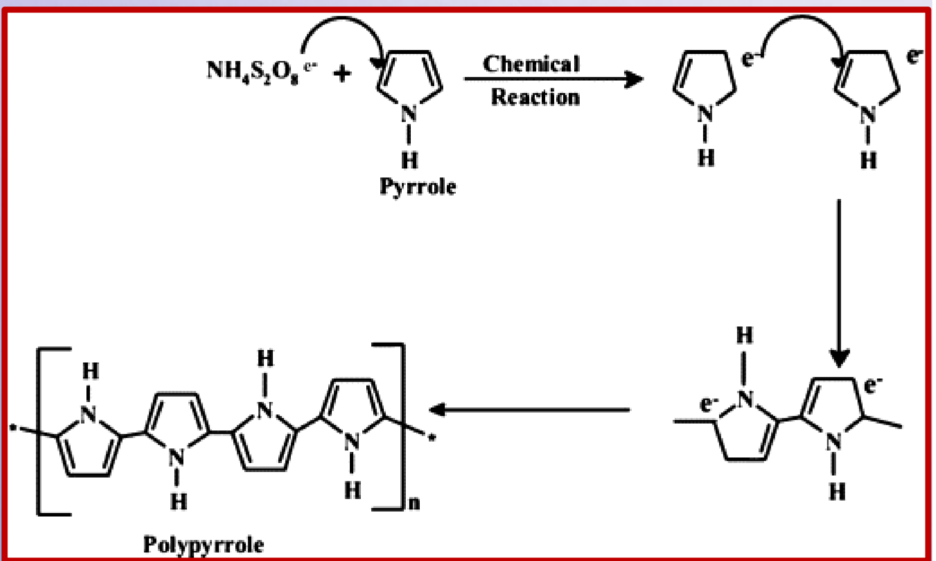


Polyaniline (NH), Polyphenylene sulfide (S)

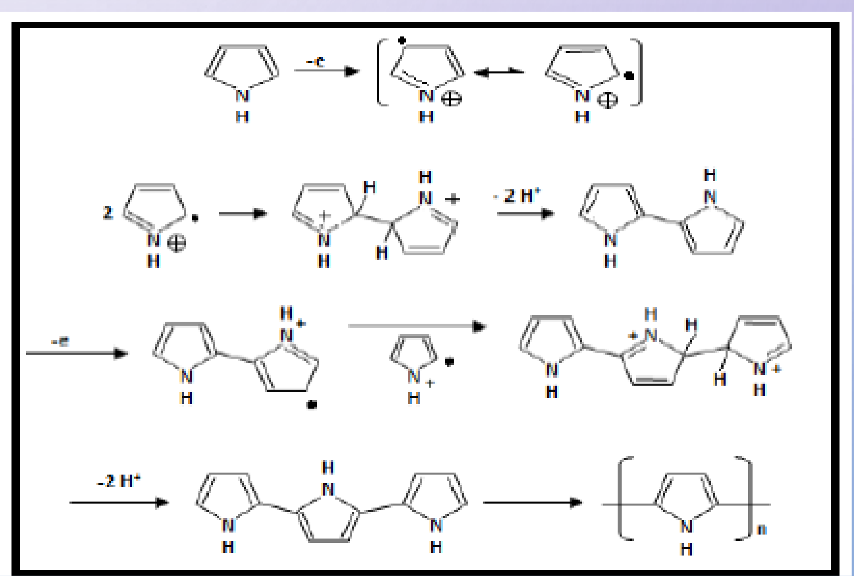
Polypyrrole



Polypyrrole (PPy): The conduction mechanism of PPy is shown in scheme. Polypyrrole can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer. Oxidative polymerisation of pyrrole to PPy proceeds via a one electron oxidation of pyrrole to a radical cation, which subsequently couples with another radical cation to form the 2,2'- bipyrrole. This process is then repeated to form longer chains of Polypyrrole.

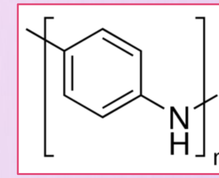


Chemical methods

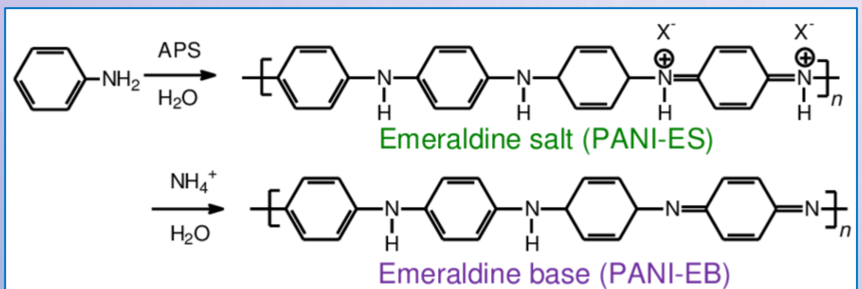


Electrochemical methods

Polyaniline

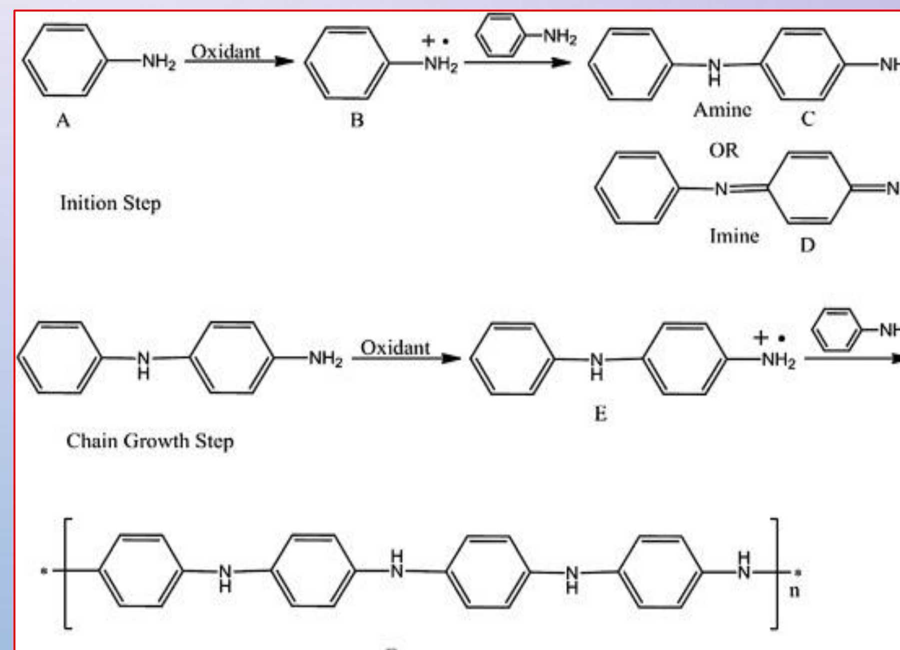


Polyaniline (PANI): The mechanism of formation of PANI is shown in scheme below. Polymerization of aniline involves oxidation of aniline monomer to form dimeric species as the oxidation potential of aniline is higher than those of dimers, subsequently formed oligomers and polymers. Upon creation, the dimers are immediately oxidized and then react with an aniline monomer via an electrophilic aromatic substitution, followed by further oxidation and deprotonation to afford the trimers. This process is repeated, eventually leads to the formation of Polyaniline.

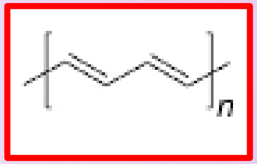


APS: Ammonium Persulfate

Mechanism of formation of polyaniline

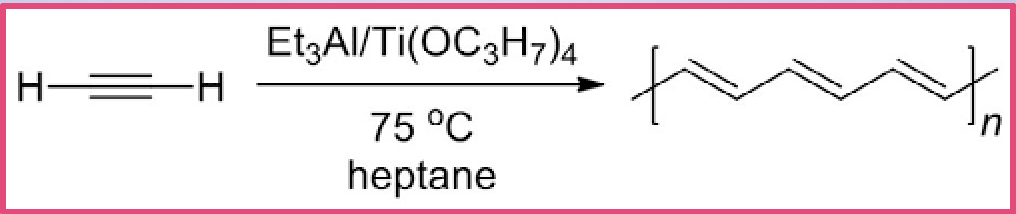


Polyacetylenes



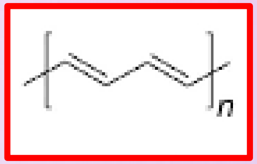
Polyacetylenes: The polyacetylene film forms at the gas-liquid interface when acetylene gas passes through a heptane solution of the Ziegler-Natta catalyst. Cis polymer forms at low temperature (-78 °C). Isomerization to the more stable trans form takes place on rising the temperature of the film. Conductivity of doped cis films is two or three times greater than the trans analogues.

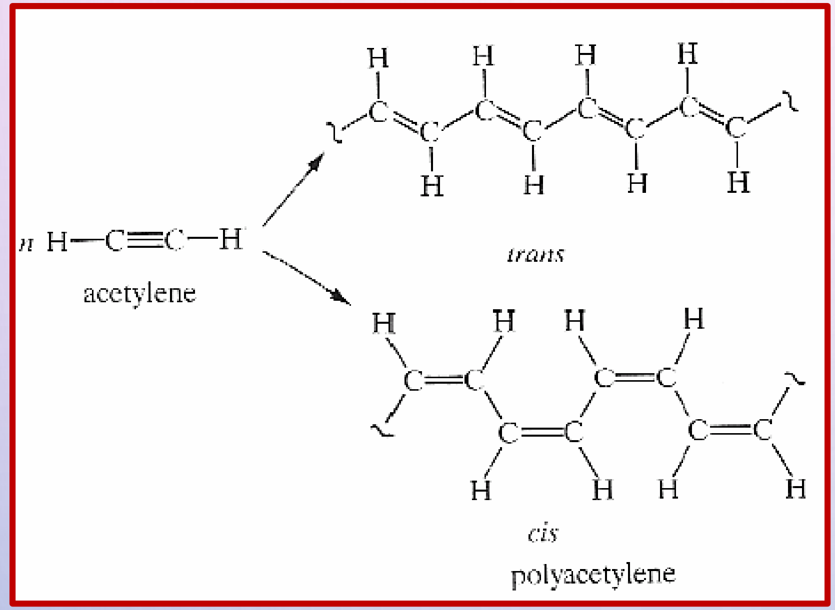
Hideki Shirakawa awarded 2000 Nobel prize jointly with Alan J. Heeger, Alan G. MacDiarmid for the discovery and developments on conductive polymers



Polyacetylene (CH)x

Polyacetylenes





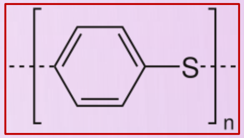
High Temperature form(100^{0}C)

Low Temperature form(-80^{0}C)

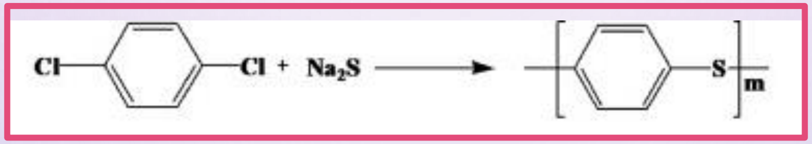
Although the application of polyacetylene is limited but the discovery of this conductive organic polymer lead to the development in the area of research, of material science .

Applications: Doped Polyacetylene offers a good electrical conductivity, hence can be used as electrode material in light weight rechargeable batteries. I_3-dopped acetylene can also be used in biosensors.

Polyphenylene sulfide



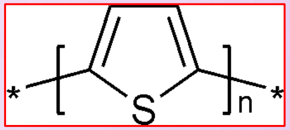
Polyphenylene sulfide (PPS) is an organic conductive polymer having aromatic rings attached by sulfide (-S-) linkage. The PPS (polyphenylene sulfide) polymer is formed by reaction of Na_2S with p-dichlorobenzenes.



PPS is used in filter fabric for coal boilers, papermaking felts, electrical insulation, film capacitors, specialty membranes, gaskets, and packings. The PPS, which is otherwise insulating, can be converted to the semiconducting form by oxidation or use of dopants.

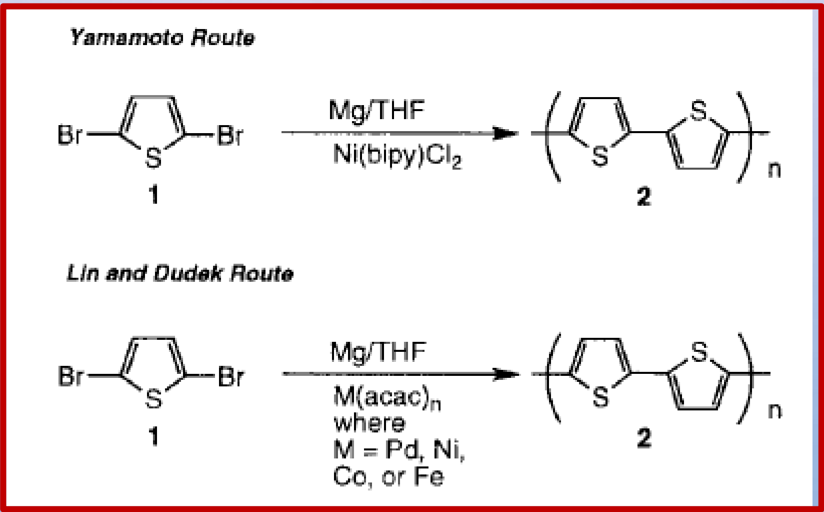
Polyphenylene sulfide is an engineering plastic, commonly used today as a high-performance thermoplastic. PPS can be molded, extruded, or machined to tight tolerances.

Polythiophene

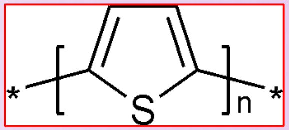


Polythiophenes (PTs): Polythiophenes are polymerized thiophenes, a five membered sulfur heterocycle.

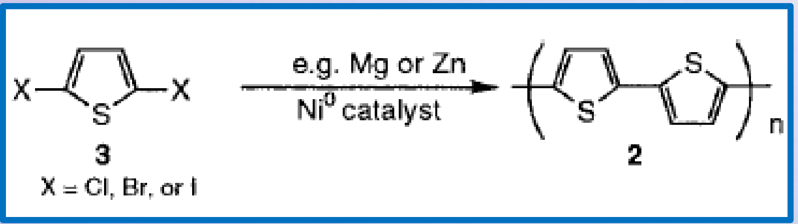
Unsubstituted polythiophene were synthesized by a metal-catalyzed polycondensation polymerization of 2,5-dibromothiophene (1). Yamamoto's synthesis treats 2,5-dibromothiophene with Mg in tetrahydrofuran (THF) in the presence of nickel(bipyridine) dichloride. The Mg reacts with either bromide to form either 2-bromo-5 magnesiobromothiophene or 2-magnesiobromo-5-bromothiophene, which is self-coupled with the Ni(II)- catalyst to form a thiophene dimer carrying a MgBr at one end and a Br at the other.



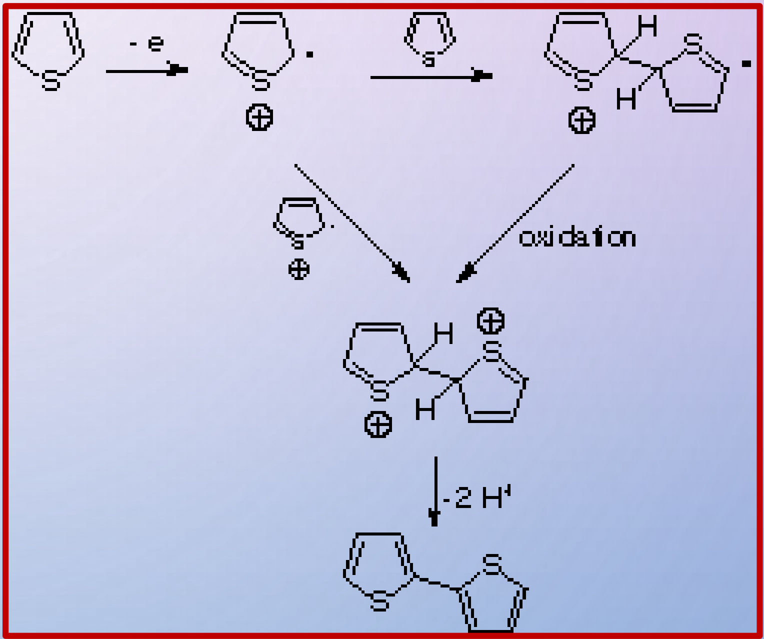
Polythiophene



The 2,5-dihalothiophene can be polymerized by a polycondensation dehalogenation reaction with Ni(0). The polythiophene can also be synthesized by electrochemical method. In an electrochemical polymerization, a solution containing thiophene and an electrolyte produces a conductive Polythiophene film on the anode.

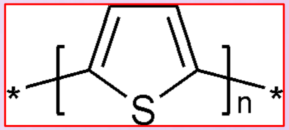


Mechanism of formation of polythiophene

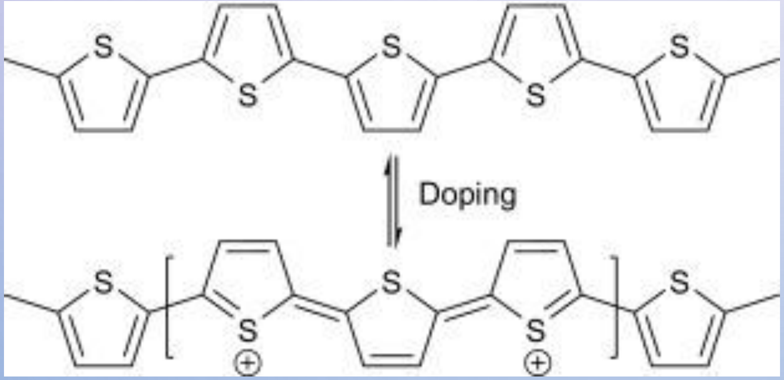


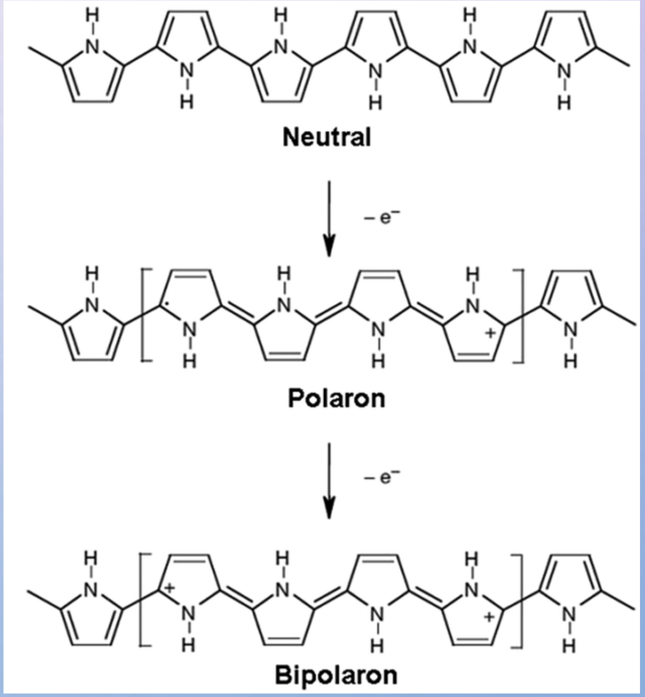
PTs become conductive when it is oxidized. The electrical conductivity results from the delocalization of electrons along the polymer backbone. Conductivity however is not the only interesting property resulting from electron delocalization.

Polythiophene

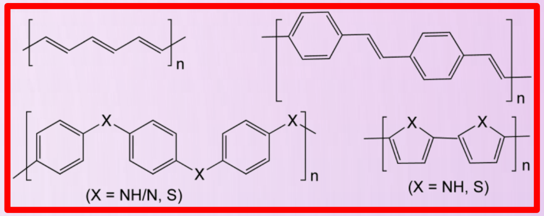


Applications of polythiophene: Polythiophenes are most environmentally and thermally stable materials that can be used as electrical conductors, nonlinear optical devices, polymer LEDs, electrochromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, electrodes, microwave absorbing materials, new types of memory devices, nanoswitches, optical modulators and valves, imaging materials, nanoelectronic and optical devices, and transistors.

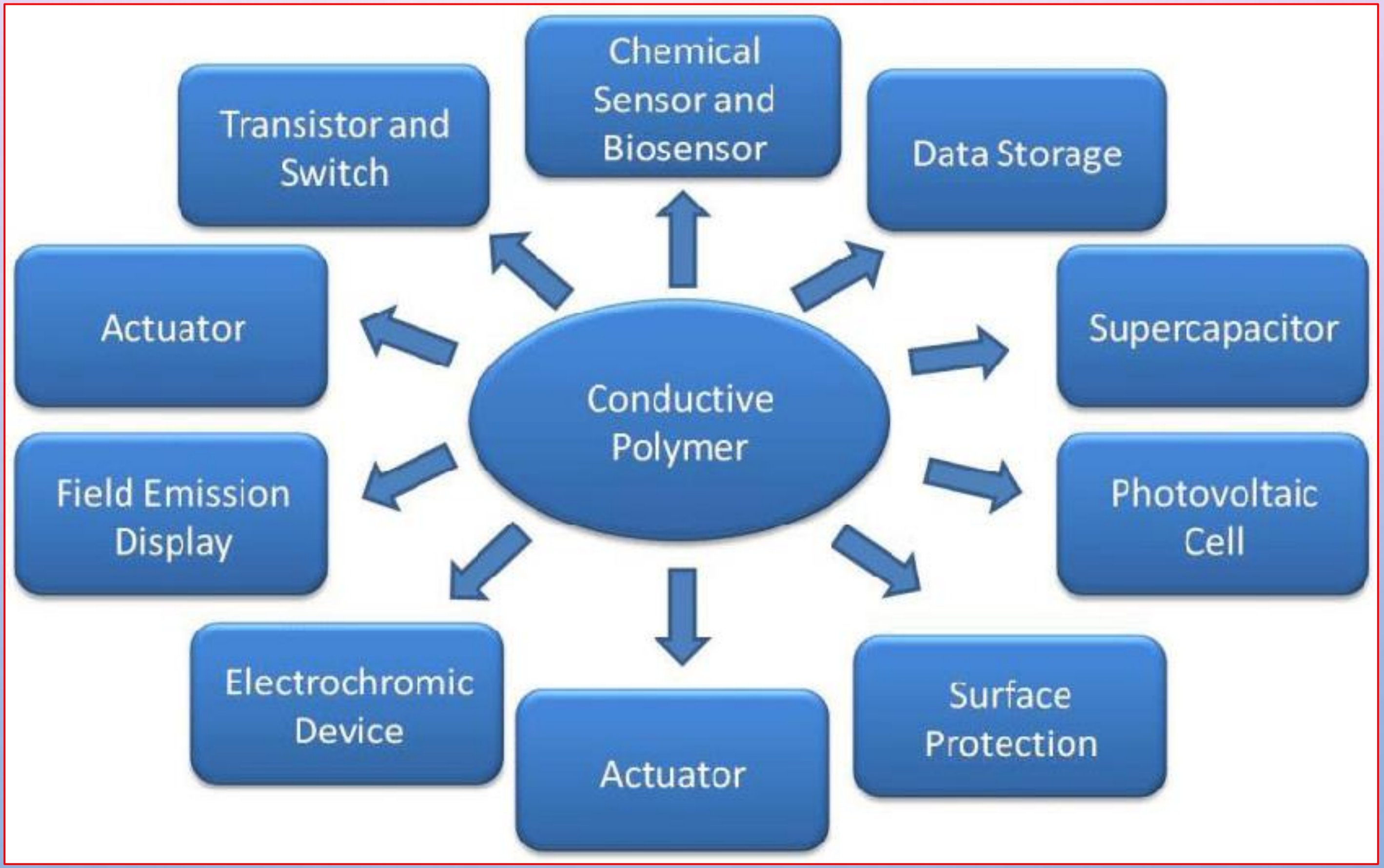




Conductive Polymers



Applications of conductive Polymers



References and suggestions for further reading:

1. Textbook of Polymer Science by Fred W. Billmeyer, Wiley

2. Zh. A. Boeva and V. G. Sergeyev, Polymer Science Series C, Vol. 56 No. 1 2014.

3. R. D. McCullough, Advance Materials. 1998, 10, No. 2

THANK YOU