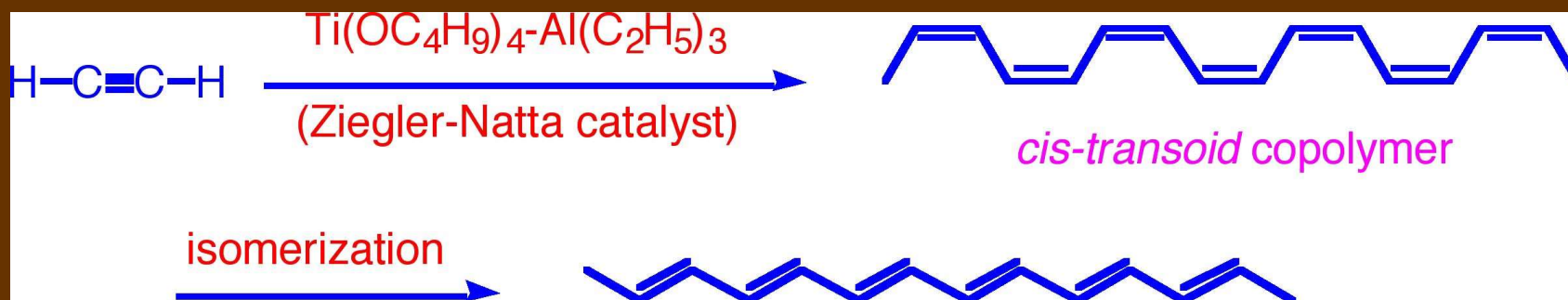


# Synthesis of Polyacetylene

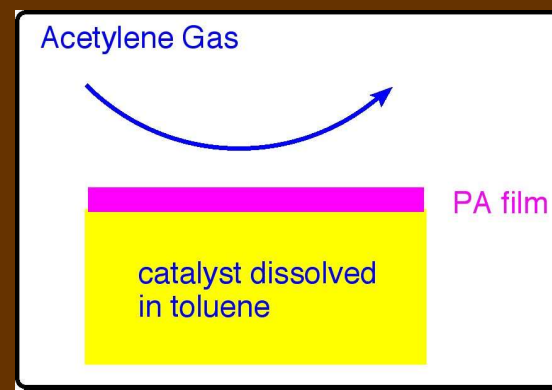
by Ziegler-Natta Catalyst



Effect of Temperature:

At  $-78^\circ\text{C}$  or below: all-*cis* PA

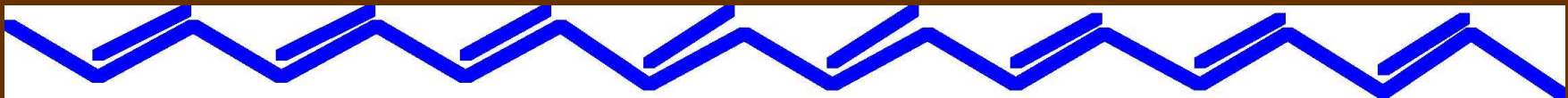
At  $180^\circ\text{C}$  or higher: all-*trans* PA



## Polymers with Unsaturated (Conjugated) backbone structure

- A conjugated main chain with alternating single and double bonds with delocalized electrons
- First example of conjugated polymer: Polyacetylene
- Conducting polymers can be intrinsically conducting polymers, doped conducting polymers or extrinsically conducting polymers
- Pure polyacetylene:  $\sigma \sim 10^{-9}$  (*cis*) and  $10^{-5}$  (*trans*) S cm<sup>-1</sup>. High electrical conductivity was observed when the polymer was “**doped**” with oxidizing or reducing agents

*Trans* polyacetylene

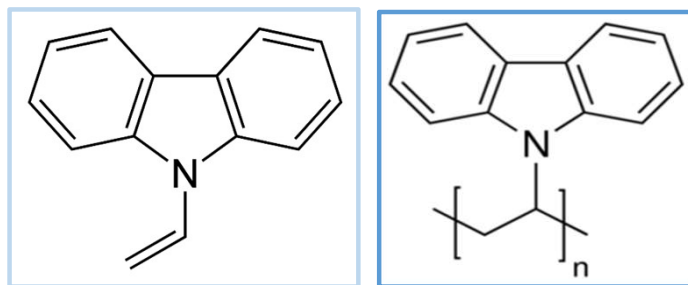


# Polymerization of cis and trans stilbene

- Polymerization of cis and trans stilbene results in different types of polymers due to geometrical structural difference between the isomers.
- **1. Cis-Stilbene Polymerization:**
  - - Cis-stilbene has two phenyl rings on the same side of the double bond.
  - - Polymerization of cis-stilbene typically leads to **atactic polymers**. In atactic polymers, the side groups or substituents are randomly oriented along the polymer chain, resulting in a lack of regularity or order in the polymer structure.
  - - The random arrangement of side groups in atactic polymers leads to amorphous materials with properties such as low crystallinity, low melting points, and reduced mechanical strength compared to isotactic or syndiotactic polymers.
  -
- **2. Trans-Stilbene Polymerization:**
  - - Trans-stilbene has two phenyl rings on opposite sides of the double bond.
  - - Polymerization of trans-stilbene can lead to **isotactic or syndiotactic polymers**, depending on the conditions and catalysts used.
  - - Isotactic polymers have side groups arranged predominantly on the same side of the polymer backbone, resulting in a more ordered and crystalline structure. This arrangement often leads to improved mechanical properties and higher melting points compared to atactic polymers.
  - - Syndiotactic polymers have alternating side groups along the polymer chain, leading to a different type of regularity and crystallinity compared to isotactic polymers.
- **DRAW THE CHEMICAL STRUCTURES BY YOURSELF AS PART OF CLASS DISCUSSION**
- In summary, the difference in the polymerization of cis-stilbene and trans-stilbene lies in the structure and arrangement of side groups along the polymer chain, resulting in polymers with different properties such as crystallinity, melting points, and mechanical strength.

# Semiconducting / Photoconducting Polymers

- Characterized by its photoconductivity when exposed to light
- Poly(*N*-vinylcarbazole) (PVK) polymer with active carbazole pendant group is an excellent example
- Prepared from *N*-vinyl carbazole
- Pure PVK is a hole conductor with dark conductivity of  $\sim 10^{-14} \text{ S cm}^{-1}$
- The photoconductivity of PVK is found to be  $\sim 10^{-7}$  to  $10^{-6} \text{ S cm}^{-1}$
- It is the first reported photoconducting polymer material



## Advantages and Properties:

Economical, byproducts from petroleum industry cracking.

Development of value added products in modern day materials science and electronics application.

Conducting polymers, PVK and other carbazole containing compounds have high thermal stability (170 deg C) and photochemical stability.

Application in optoelectronic devices.

Carbazole containing polymers can be easily functionalized.

Charge transport, optically active, thermal stability, self-assembly and good morphology.

Band gap of the resulting polymer can also be tuned.

Certain carbazole containing compounds exhibit high carrier mobilities.

Higher conductivity and enhanced carrier mobilities.

Polymers containing carbazole groups are electron rich and are used as hole transport materials in various optoelectronic device applications.

## **Applications:**

### **Organic / polymer based devices**

Light emitting diodes (One of the major applications)

Photovoltaic cells including flexible devices (All kinds of solar cell applications such as DSSC, OPV or PSC, hybrid perovskite solar cells)

Photodetectors

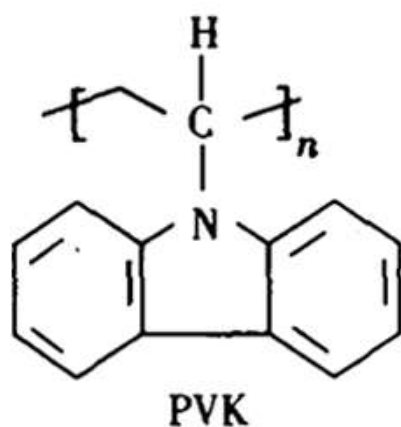
Photorefractive materials (due to its photoconducting behavior)

Electrophotography or xerography applications including laser printers

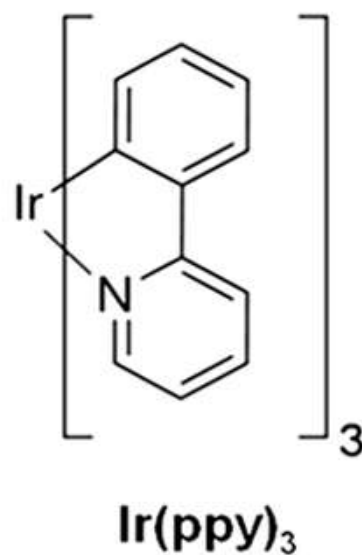
Field effect transistors

Resistive devices and sensors

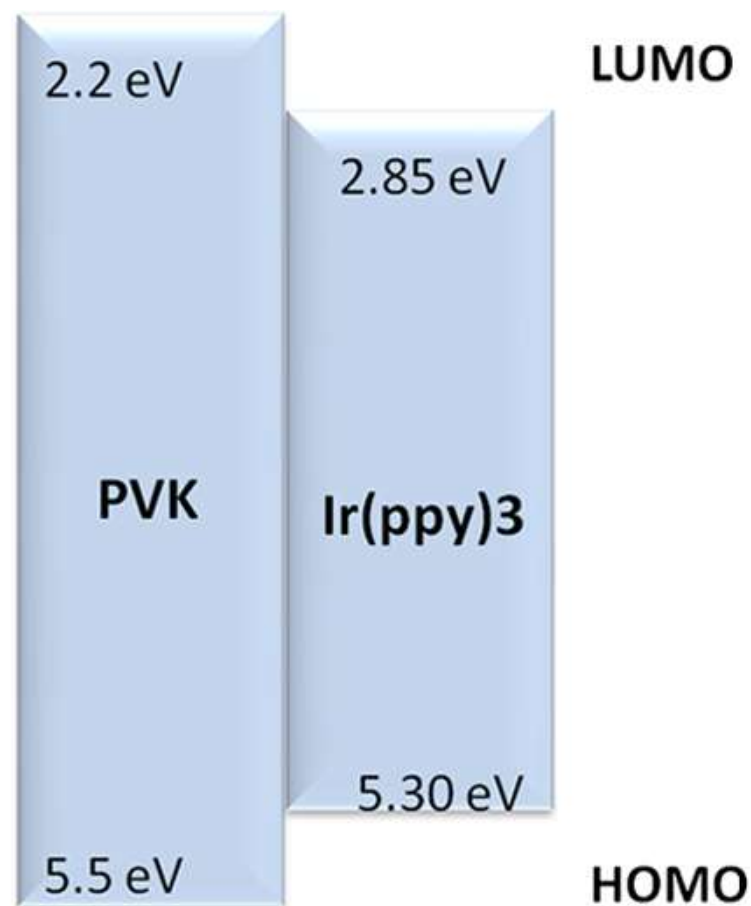
## GREEN PHOSPHORESCENT LED



(a)



(b)



Q. Explain the structures, HOMO-LUMO energy levels and band gap of PVK and  $\text{Ir(ppy)}_3$  and their likely application.

# GREEN PHOSPHORESCENT LED

Green phosphorescent organic light-emitting diodes (OLEDs) based on the well-known host 4,4-dicarbazol-9-yl-biphenyl and the green phosphor emitter *fac* tris-2-phenylpyridinato-N,C-2-iridium – Ir(ppy)<sub>3</sub>.

A spin-coated hole-injection/transport layer of poly-N-vinyl-carbazole and a green-emitting and dopant material based on iridium were used to fabricate a green LED device in a simplified device geometry that requires the deposition of only two organic layers from the vapor phase.

Device architecture was glass/ITO/PEDOT:PSS/PVK + Ir(ppy)<sub>3</sub>-active layer/LiF/Al.

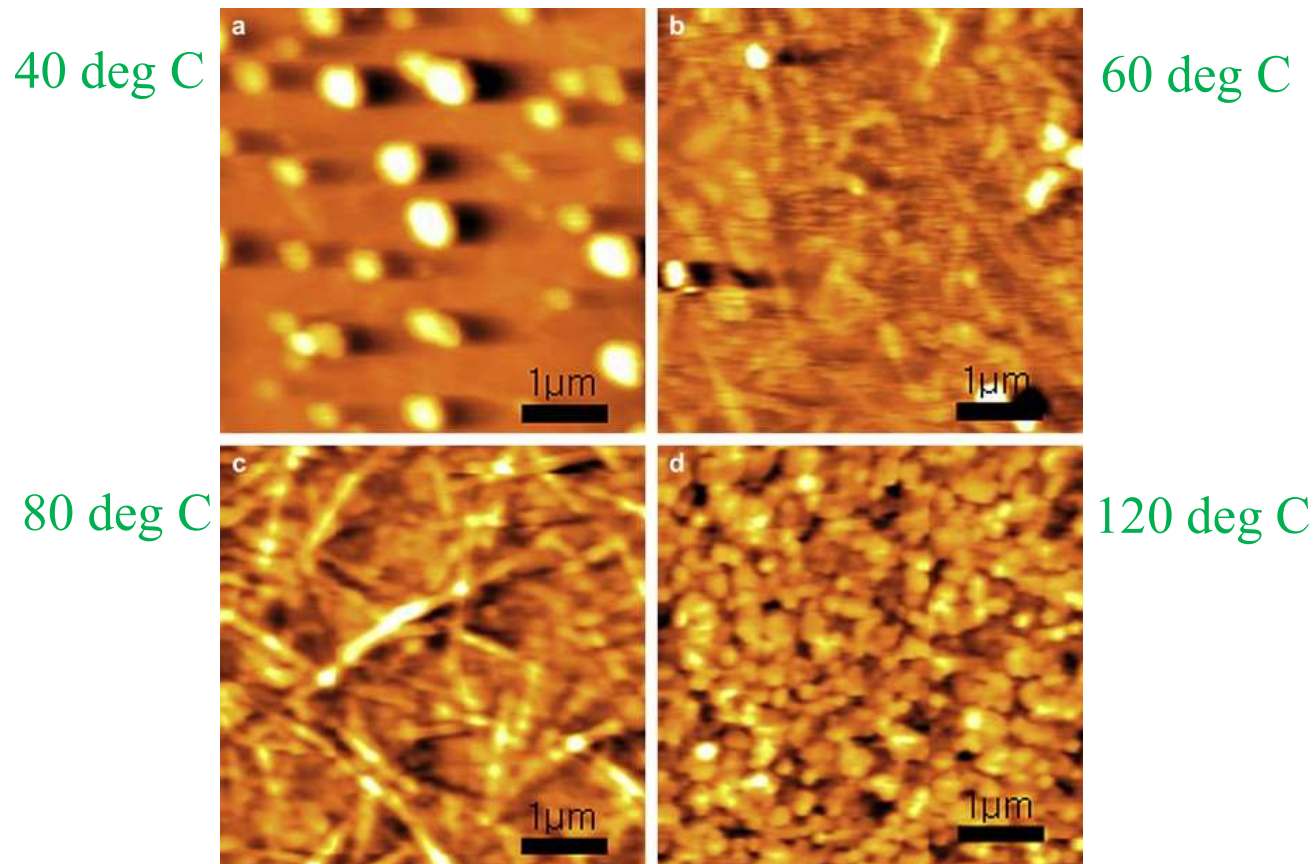
Device active layer was *Gravure* printed on the substrate. (*Gravure*-next slide).

Thermal annealing helps in reducing roughness and rearranging polymer molecules to form linear structure.

Optimum temperature is determined around 80 °C for the PVK and Ir(ppy)<sub>3</sub> gravure printed organic layers in this work.



## AFM Images of *Gravure* printed devices

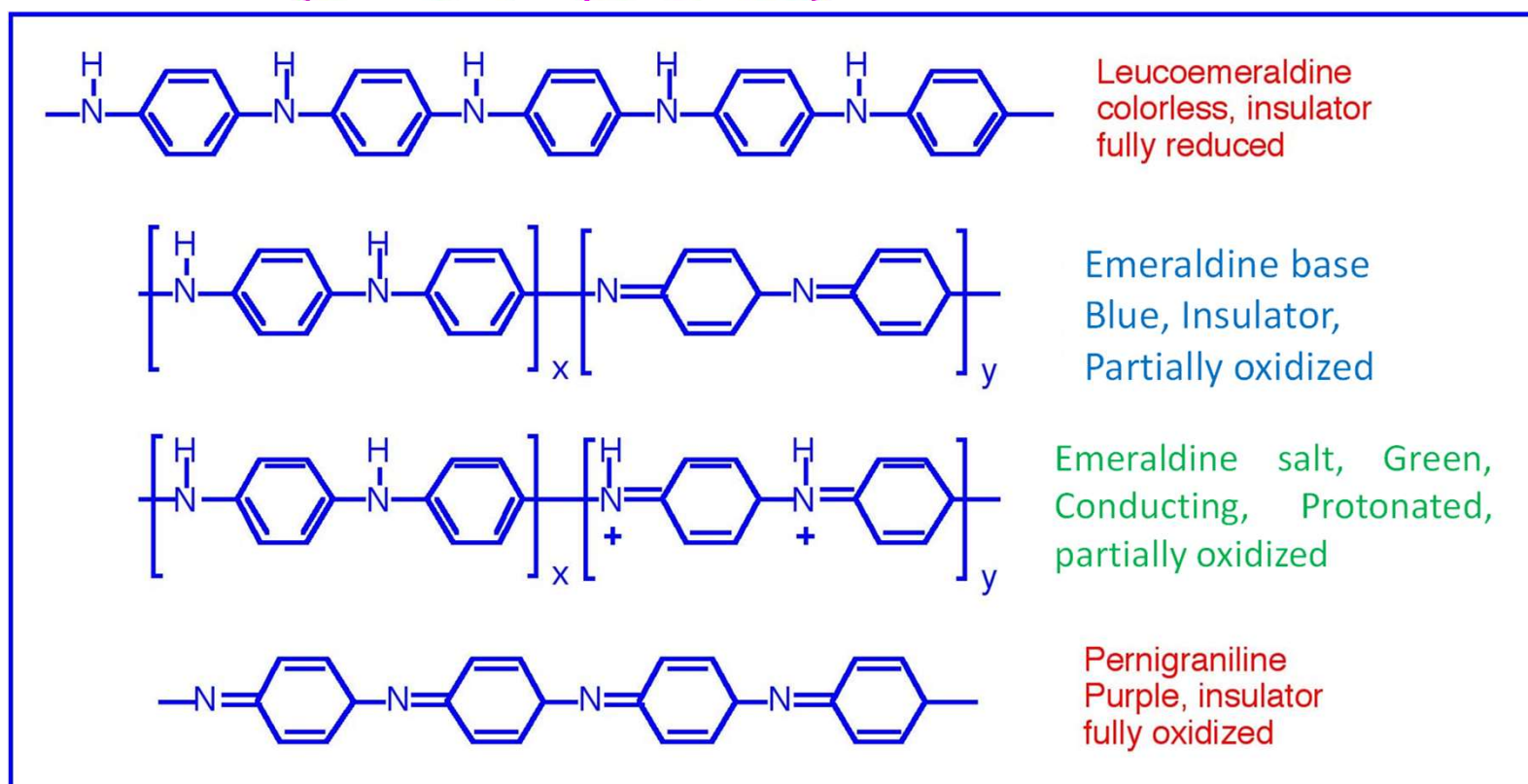
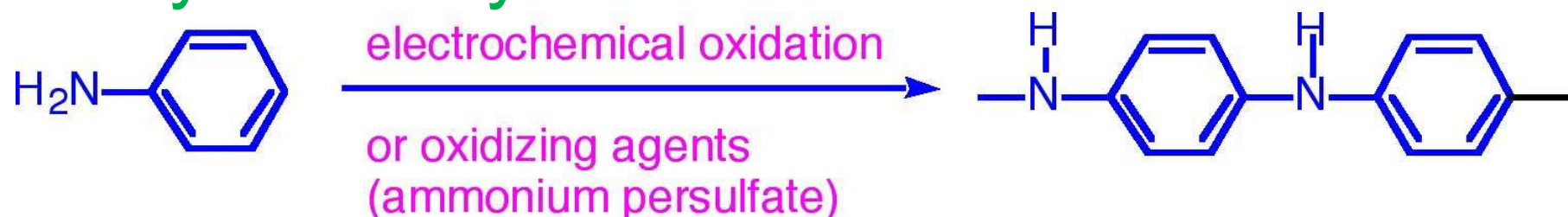


*Gravure* is a printing method in which an image is applied to a printing substrate by use of a metal plate mounted on a cylinder. Unlike other processes, *gravure* uses a depressed or sunken surface for the desired image.

## Polyaniline-abbreviated as PANI or PAni

- An important conducting polymer that is also the oldest.
- Can be grown by using aqueous and non-aqueous route.
- Can be obtained by electrochemical synthesis or oxidative coupling of aniline.
- New device technologies for sensors and anticorrosion.
- Doping achieved by adding protonic acid.
- Aniline used to prepare PANI - Several forms: leucoemeraldine, emeraldine, emeraldine salt, pernigraniline.
- Reversible redox behavior-supercapacitor, sensors, fuel cells, coatings, EM shielding.
- Structure can be tuned as desired.

# Polyaniline synthesis and its different forms



# Polyaniline unique properties

Band gap can be tuned from 4.3 eV to 2.6 eV in the reduced and oxidized forms.

It has very high thermal, and electrical conductivity as well as high environmental, chemical and electrochemical stability.

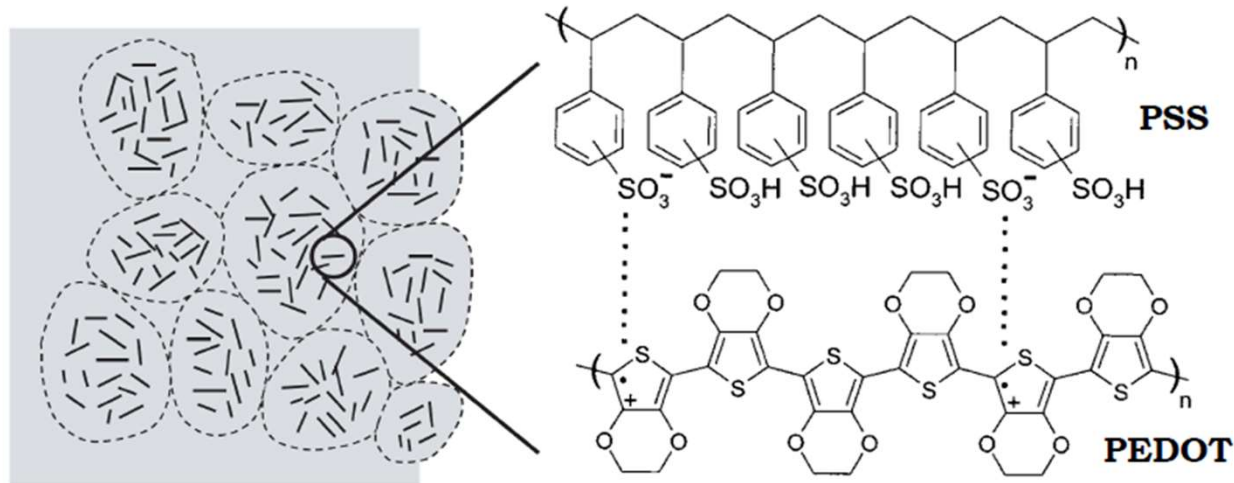
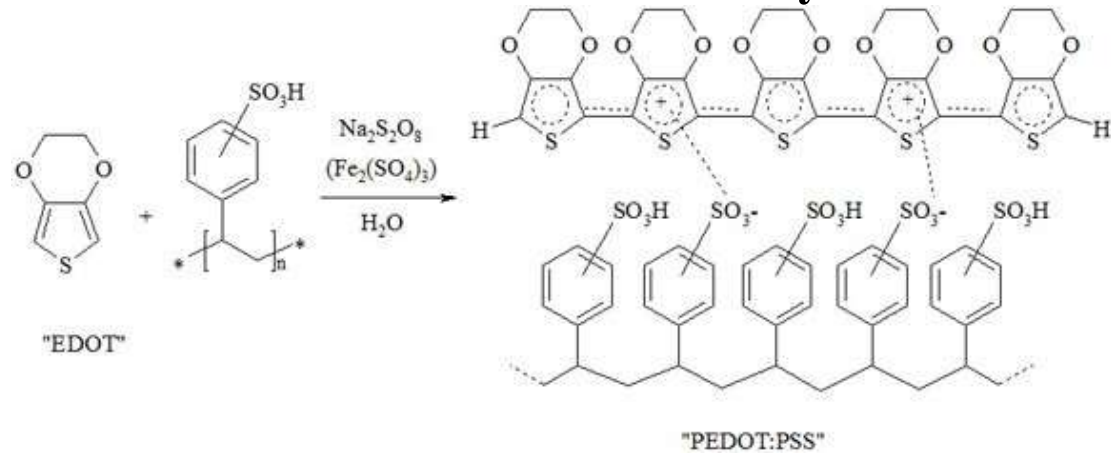
PANI can be used as conducting polymer to fabricate functionalized nanocomposites with inorganic salts and organic nanomaterials.

PANI exists as nanoparticles, nanosheets, nanotubes, nanorods, nanowires, nanoplates, and nanowhiskers have been developed with PANI.

Ultrathin films (in nanometer range) can be prepared by PANI on any surfaces and be used as devices.

The colour change associated with polyaniline in different oxidation states can be used in sensors and electrochromic devices.

## PEDOT:PSS Structure and Synthesis



Left image represents the top view morphology of thin film of PEDOT:PSS particles surrounded by a thin PSS-rich surface layer. Right image is the chemical structure of the species present in the film

## Properties of PEDOT:PSS

PEDOT is an important and a relatively new member in the conducting-polymer family (HOMO~ -5.0 eV)

Good electrochemical, ambient, and thermal stability of its electrical properties as compared with that of other polythiophenes.

PEDOT is built from ethylenedioxythiophene (EDOT) monomers and PSS as a template polymer using sodium peroxodisulfate as the oxidizing agent.

The role of PSS, which has a much higher molecular weight, is to act as the counter ion and to keep the PEDOT chain segments dispersed in the aqueous medium.

It is insoluble in many common solvents and unstable in its neutral state, as it oxidizes rapidly in air.

## Properties of PEDOT:PSS

To improve its processability, a polyelectrolyte solution (PSS) can be added, and this results in an aqueous dispersion of PEDOT:PSS, where PEDOT is its oxidized state.

Each phenyl ring of the PSS monomer has one acidic  $\text{SO}_3\text{H}$  (sulfonate) group.

This affords PEDOT in its highly conducting ( $10^{-3}$  S/cm), cationic form.

PEDOT is a collection of oligomers with lengths up to  $\sim 20$  repeating units.

In general PEDOT:PSS gel particles are formed that possess excellent processing characteristics to make thin, transparent, conducting films.



## **Applications of PEDOT:PSS**

It has very wide applications in energy conversion and storage devices, especially in OLED and photovoltaic devices.

PEDOT:PSS is also used in flexible and stretchable electronic devices.

Highly conducting polymer can be obtained by various methods like doping and preparing composites with other materials.

PEDOT:PSS is also useful as a conducting hydrogels for tissue engineering and biomedical applications.

Large area devices with PEDOT:PSS gel particles are utilized to form transparent thin films for optoelectronic device applications.

Recently, thermoelectrical properties of PEDOT:PSS have also been reported.