Conducting Polymers

- Discovered in 1963
- Most recent generation of polymers
- Characterised by conjugated bonds
- There are other types of organic conductors

, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa, 2000 Nobel
Overlap of delocalised pi electrons along polymer backbone
Since most organic polymers do not have intrinsic charge carriers, the required charge carriers may be provided by partial oxidation (p-doping) of the polymer chain with electron acceptors (e.g. I, AsF₅) or by partial reduction (n-doping) with electron donors (e.g. Na, K). Through such a doping process, charged defects (e.g. polaron, bipolaron and soliton) are introduced, which could then be available as the charge carriers.
They are semiconductors/dielectrics in the neutral state

• To conduct the polymers need to undergo a redox reaction
• When oxidised the chain becomes positively charged
• This occurs either chemically or electrochemically
• The process is called doping and introduces charge defects called polarons
• Oxidation: p type doping (I₂ is the electron acceptor), which the most common
• Reduction: n type doping (Na)
When an electron is added to the bottom of the conduction band (from the top of the valence band) of a conjugated polymer the conduction band ends up being partially filled and a radical anion, commonly termed as a polaron, is created. The formation of polarons causes the injection of states from the bottom of the conduction band and top of the valence band into the band gap. The process is called DOPING.
Polaron: a loosely held but localised electron surrounded by a lattice distortion.

Fig. 6. A simplified explanation of the electrical conductivity of conducting polymers. (A) The dopant removes or adds an electron from/to the polymer chain, creating a delocalized charge. (B) It is energetically favourable to localize this charge and surround it with a local distortion of the crystal lattice. (C) A charge surrounded by a distortion is known as a polaron (a radical ion associated with a lattice distortion [63]). (D) The polaron can travel along the polymer chain, allowing it to conduct electricity.
<table>
<thead>
<tr>
<th>Polymer (date conductivity discovered)</th>
<th>Structure</th>
<th>$\varepsilon_{\text{gap}}$ (eV)</th>
<th>Conductivity $#^*$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Polyacetylene and analogues</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyacetylene (1977)</td>
<td><img src="image1" alt="Structure" /></td>
<td>1.5</td>
<td>$10^3 - 1.7 \times 10^5$</td>
</tr>
<tr>
<td>Polypyrrole (1979)</td>
<td><img src="image2" alt="Structure" /></td>
<td>3.1</td>
<td>$10^2 - 7.5 \times 10^3$</td>
</tr>
<tr>
<td>Polythiophene (1981)</td>
<td><img src="image3" alt="Structure" /></td>
<td>2.0</td>
<td>$10 - 10^3$</td>
</tr>
<tr>
<td>II. Polyphenylene and analogues</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(paraphenylene) (1979)</td>
<td><img src="image4" alt="Structure" /></td>
<td>3.0</td>
<td>$10^2 - 10^3$</td>
</tr>
<tr>
<td>Poly(p-phenylene vinylene) (1979)</td>
<td><img src="image5" alt="Structure" /></td>
<td>2.5</td>
<td>$3 - 5 \times 10^3$</td>
</tr>
<tr>
<td>Polyaniline (1980)</td>
<td><img src="image6" alt="Structure" /></td>
<td>3.2</td>
<td>$30 - 200$</td>
</tr>
</tbody>
</table>

$\#^*$ The range of conductivities listed is from that originally found to the highest values obtained to date (after Dai, 1999, copyright 1999 Marcel Dekker, Inc.)
Conductivity of polyacetylene as a function of dopant concentration (Iodine)
Properties

• Brittle in neutral state
• Usually black
• Easy to process
• Not thermoplastic
• They are synthesised easily and can be doped during synthesis
• Doping is usually done electrochemically, in water
• Counterions are also involved
• Infinitely tunable
DOPING

• Chemical
• Electrochemical
• Photodoping
Applications

• Sensing
• Actuation
• Release
• Highly biocompatible

Ref: Balint et al Acta Biomaterialia, 10 (2014) 2341
Dendritic polymers

(a)

(b)

(c)
Their many applications depend on their properties.
Naso Artificiale, e-nose, e-tongue

• Elencare le differenze tra e-nose e e-tongue
• Elencare le applicazioni
• Progettare un Sistema per un sensore di sapore. Da considerare: metodo di trasduzione, materiali da usare, connessioni, configurazione e campo di applicazione