

## CONDUCTING POLYMERS

**Conductive polymers** or, more precisely, **intrinsically conducting polymers (ICPs)** are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

The linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers are the main class of conductive polymers. Poly(p-phenylene vinylene) (PPV) and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) are the archetypical materials for solar cells and transistors.

<ul style="list-style-type: none"> <li>• <i>Poly(fluorene)s</i></li> <li>• <i>polyphenylenes</i></li> <li>• <i>polypyrenes</i></li> <li>• <i>polyazulenes</i></li> <li>• <i>polynaphthalenes</i></li> </ul>	<p>The N is in the aromatic cycle:</p> <ul style="list-style-type: none"> <li>• <b>poly(pyrrole)s(PPY)</b></li> <li>• <i>polycarbazoles</i></li> <li>• <i>polyindoles</i></li> <li>• <i>polyazepines</i></li> </ul>	<p>The S is in the aromatic cycle:</p> <ul style="list-style-type: none"> <li>• <b>poly(thiophene)s (PT)</b></li> <li>• <b>poly(3,4-ethylenedioxythiophene)(PEDOT)</b></li> </ul>
	<p>The N is outside the aromatic cycle:</p> <ul style="list-style-type: none"> <li>• <b>polyanilines (PANI)</b></li> </ul>	<p>The S is outside the aromatic cycle:</p> <ul style="list-style-type: none"> <li>• <b>poly(p-phenylene sulfide)(PPS)</b></li> </ul>
<p>Double bonds</p>	<ul style="list-style-type: none"> <li>• <b>Poly(acetylene)s(PAC)</b></li> </ul>	

The conductivity of such polymers is the result of several processes. For example, in traditional polymers such as polyethylenes, the valence electrons are bound in  $sp^3$  hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material. However, in conjugated materials, the situation is completely different. Conducting polymers have backbones of contiguous  $sp^2$  hybridized carbon centers. One valence electron on each center resides in a  $p_z$  orbital, which is orthogonal to the other three sigma-bonds. All the  $p_z$  orbitals combine with each other to a molecule wide delocalized set of orbitals. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus, the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. The band structures of conductive polymers can easily be calculated with a tight binding model. In principle, these same materials can be doped by reduction, which adds electrons to an otherwise unfilled band. In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction silicon atoms are replaced by electron-rich, *e.g.*, phosphorus, or electron-poor, *e.g.*, boron, atoms to create n-type and p-type semiconductors, respectively.

Although typically "doping" conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped."

Undoped conjugated polymers state are semiconductors or insulators. In such compounds, the energy gap can be  $> 2$  eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around  $10^{-10}$  to  $10^{-8}$  S/cm. Even at a very low level of doping ( $< 1\%$ ), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm. Although the pi-electrons in polyacetylene are delocalized along the chain, pristine polyacetylene is not a metal. Polyacetylene has alternating single and double bonds which have lengths of 1.44 and 1.36 Å, respectively. Upon doping, the bond alteration is diminished in conductivity increases. Non-doping increases in conductivity can also be accomplished in a field effect transistor (organic FET or OFET) and by irradiation. Some materials also exhibit negative differential resistance and voltage-controlled "switching" analogous to that seen in inorganic amorphous semiconductors.

Despite intensive research, the relationship between morphology, chain structure and conductivity is still poorly understood. Generally, it is assumed that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains, however this could not be confirmed for polyaniline and was only recently confirmed for PEDOT, which are largely amorphous.

#### Properties and applications

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Due to their poor processability, conductive polymers have few large-scale applications. They have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors and biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Another use is for microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, augment this field with their higher surface area and better dispersability.

With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

#### **Electroluminescence**

light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern

conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

### **Barriers to applications**

Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis.

Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can only be processed by dispersion.

### **Polymeric membranes**

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments. The main advantages of membrane technology as compared with other unit operations in (bio)chemical engineering are related to this unique separation principle, i.e. the transport selectivity of the membrane. Separations with membranes do not require additives, and they can be performed isothermally at low temperatures and—compared to other thermal separation processes—at low energy consumption. Also, upscaling and downscaling of membrane processes as well as their integration into other separation or reaction processes are easy.

Polymeric membranes lead the membrane separation industry market because they are very competitive in performance and economics. Many polymers are available, but the choice of membrane polymer is not a trivial task. A polymer has to have appropriate characteristics for the intended application. The polymer sometimes has to offer a low binding affinity for separated molecules (as in the case of biotechnology applications), and has to withstand the harsh cleaning conditions. It has to be compatible with chosen membrane fabrication technology. The polymer has to be a suitable membrane former in terms of its chains rigidity, chain interactions, stereoregularity, and polarity of its functional

groups. The polymers can form amorphous and semicrystalline structures (can also have different glass transition temperatures), affecting the membrane performance characteristics. The polymer has to be obtainable and reasonably priced to comply with the low cost criteria of membrane separation process. Many membrane polymers are grafted, custom-modified, or produced ascopolymers to improve their properties.<sup>[4]</sup> The most common polymers in membrane synthesis are cellulose acetate, Nitrocellulose, and cellulose esters (CA, CN, and CE), polysulfone (PS), polyether sulfone(PES) ,polyacrilonitrile (PAN) , polyamide , polyimide, polyethylene and polypropylene (PE and PP), polytetrafluoroethylene(PTFE), polyvinylidene fluoride (PVDF), polyvinylchloride (PVC).

Some commonly used polymers in membrane technology are polysulfone (PSF), polyethersulfone (PES), polyacrilonitrile (PAN), polyamide (PA), polypolyethylene and polypropylene (PE and PP).

The choice for a particular polymer is not trivial. The selection of the right polymeric membrane depends on the application and the chemical resistance level required in your separation process.