Lecture 6

Polymers

A polymer is a large molecule made of a chain of individual basic units called monomers joined together in sequence. **A copolymer is a macromolecule containing two or more types of monomers.** When the polymer is a good conductor of electricity, it is referred to as conductive polymer (or organic metal). In this lecture, nanostructuring of polymers and the effect this can have on the properties of polymers are described. The focus is on copolymers since these are extremely useful in nanotechnologies.

- **Conductive polymers**

Polymers that are good conductors of electricity are called conductive polymers and include polyacetylene, polyaniline, polypyrrole, polythiophene — many more have also been synthesised. These polymers are characterised by their alternating double-single chemical bonds, so they are π-conjugated. **The π-conjugation of the carbon bonds along the oriented polymer chains provides a pathway for the flow of conduction electrons and is thus responsible for the good electrical conduction properties of the material.** A detailed SEM analysis of conductive polymers has revealed that these are made of a sequence of metallic nanoparticles about 10 nm in diameter. **The high conductivity of polymers such as polyacetylene and polyaniline is related to the nanostructure of the polymer**. **Polyaniline and its analogues change colour when a suitable voltage is applied, or when reacting with specific chemicals (electrochromic and chemochromic). For this reason, they are promising for use in light-emitting diodes (LEDs)**. Other applications are the

surface finish of printed-circuit boards, corrosion protection of metal surfaces, semi-transparent antistatic coatings for electronic products, polymeric batteries and electromagnetic shielding.

- **Block copolymers**

A copolymer is a macromolecule containing two or more types of monomers and a block copolymer comprises these basic units or monomer types joined together in long individual sequences called blocks. An example is the diblock polymer (A)m(B)n, which is made of a linear sequence of m monomers of type A joined together to a linear sequence of n monomers of type B. A transition section joints the two blocks:

[end group]-[polyA]m-[transition member]-[polyB]n-[end group]

Often, block copolymers are made of a **hydrophilic (water-attractive) block, and a hydrophobic (water-repellent) block**. In general, macromolecules having hydrophilic and hydrophobic regions, such as lipids, **self-assemble in ordered structures when in water**: the hydrophobic region packs together, avoiding the water molecules, leaving the hydrophilic molecules to the exterior of the structure. In the same way, block copolymers made of hydrophilic and hydrophobic blocks when mixed in a selective solvent, such as water, can self-assemble into ordered architectures at the nanoscale level.

The geometry and degree of order of these structures depends on the concentration and the volume ratio between insoluble and soluble blocks. Depending on these parameters, the block copolymer can form **spherical micelles (nanospheres), cylindrical micelles and membranes**. Both cylindrical and spherical micelles consist of a non-soluble (hydrophobic) core

surrounded by a soluble corona. **Membranes** are made up of two monolayers of block copolymer aligned to form a sandwich-like membrane: soluble block-insoluble block-soluble block. Molecules that, at low concentration, form spherical aggregates will assemble into cylindrical and eventually membrane-like structures as the concentration is increased.

Among spherical micelles, if the lengths of the projections formed by the hydrophilic corona are short compared to the sphere diameter, the nanostructure is called a 'hairy nanosphere', whereas if the sphere is small and the projections long, it is called a 'star polymer' (**Figure 18**).

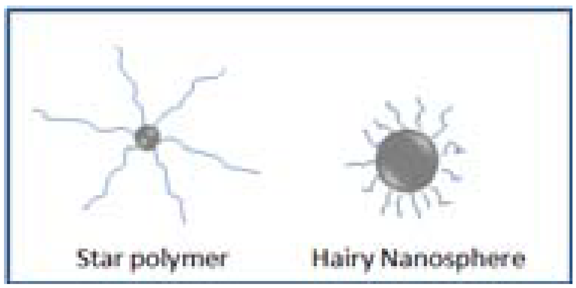

Figure 18: Sketch of a star polymer and a hairy polymer

- ## Applications of block copolymers

The application of block copolymers is not limited to the biomedical field. They can be used in conjunction with other materials to form block copolymer nanocomposites. For instance, star polymers are used in industry to **improve metal strength**.

Finally, block copolymers can form nanoporous membranes for applications in **filtering systems and fuel cell technology**.

- **Polymeric nanofibres**

Nanostructured fibrous materials, or **nanofibres**, are an important class of nanomaterials, now readily available due to recent developments in electrospinning and related fabrication technologies. In contrast to conventional woven fabrics, they have the typical structure illustrated in **Figure 19**.

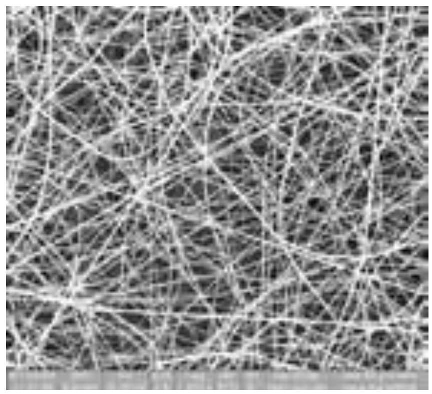

Figure 19: Typical sample of electrospun polystyrene

Nanofibres have some unique properties: they are highly porous (i.e. they have a large interconnected void volume in the range of 50 % or even greater than 90 % and possess a very high surface-to-volume ratio). It is possible to increase the mechanical stability of nanofibrous structures by annealing the fabric so to join together the crossing points of those fibres. These properties make nanofibrous scaffolds useful for many biomedical and industrial applications.

In addition, researchers have succeeded in making **coaxial nanofibres composed on two different polymers** or composite coaxial fibres. Researchers are also trying to make **aligned nanofibres**. These types of materials, particularly if made of conducting polymers, could have important applications for electronic and medical devices.

Nanofibres have a **broad spectrum of applications** as schematised in **Figure 20**.

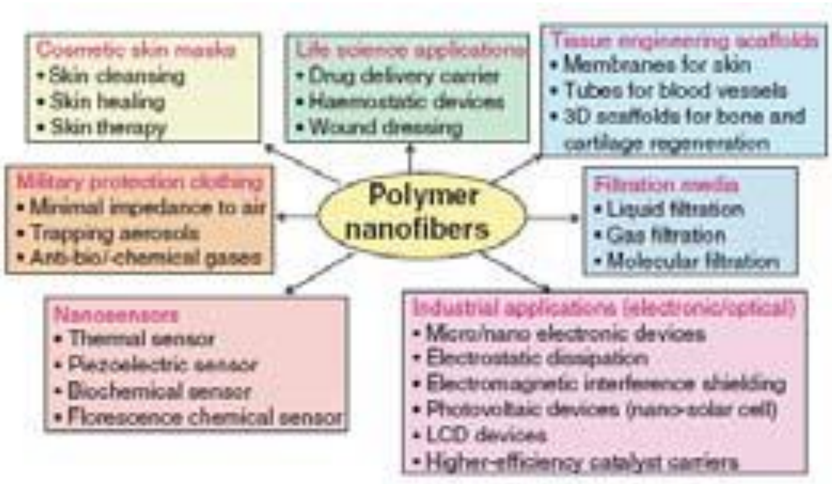

Figure 20: Overview of polymer nanofibre applications

Semiconductors

Semiconductors, unlike metals, have a band gap. The band gap is between the valence band and the conduction band. In intrinsic semiconductors which possess no impurities (e.g. boron, germanium, indium, silicon), there are no electronic states in the band gap. The properties of semiconductors, in particular the band gap, are manipulated by the addition of dopants — impurities able to donate charge carriers in the form of electrons (n-type) or holes (p-type).

As with metals, the reduction in the size of the semiconductor triggers the insurgence of novel physical properties.

Semiconducting oxides

Semiconducting oxides like TiO_2 and ZnO in bulk (macro) form are widely used in industry in many products. When they are in a nanoscale form, they display interesting physical properties that allow the design of new materials and the improvement of old. A short description of these properties follows.

Titanium dioxide

Titanium dioxide (TiO_2) is a mineral mainly found in two forms: rutile and anatase. Titanium dioxide is the most widely used white pigment because of its brightness (white colour) and very high refractive index (n = 2.4). It is used in paints, plastics, toothpastes, papers, inks, foods and medicines. **In sunscreens with a physical blocker, titanium dioxide is used both because of its high refractive index and its resistance to discolouration under ultraviolet light. This is because TiO_2 is a UV filter: it absorbs UV light**. Titanium dioxide, particularly in the anatase form, can be employed also as a photocatalyst under UV light. **It oxidises water to create hydroxyl (OH) radicals and it can also oxidise oxygen or organic materials directly. For this reason, TiO_2 is added to confer sterilising, deodorising and antifouling properties to paints, cements, windows and tiles.**

Titanium nanoparticles (30–50 nm, often referred to as **nano-TiO_2**) are at the centre of much attention due to their optical and catalytic properties: they retain the ability to absorb UV light but light scattering is dramatically reduced, so that TiO_2 goes from appearing white to transparent. **Nano-TiO_2** is thus suitable for transparent coatings, and for new-generation sunscreens, which are characterised by a high protective factor but transparent appearance. The catalytic properties of TiO_2 when nano-sized are also greatly enhanced by the large surface-to-volume

ratio. This property is increasingly used for chemical catalysis applications such as photocatalytic purification of water and air to decompose organic pollutants (solar photocatalytic remediation). Thin films of TiO_2 are used on windows to confer self-cleaning properties on the glass.

One limitation of using TiO_2 as a photocatalyst is that this material **only absorbs UV light**, which represents about 5 % of the solar spectrum. In this context, nanotechnology could bring an improvement in the form of nanoparticles with surfaces modified with organic or inorganic dyes to expand the photoresponse window of TiO_2 from UV to visible light.

- **Zinc oxide**

Zinc oxide (ZnO) has some similar properties to TiO_2 (i.e. its nanoparticles scatter light so it can be used for transparent UV filters, in creams or coatings). Like TiO_2, it is used for solar photocatalytic remediation but, compared to TiO_2, it has a weaker photocatalytic effect. Zinc oxide also suffers from the same limitation of absorbing only a fraction of the solar spectrum so research is underway to increase its photoresponse.

A peculiarity of ZnO is that it has a tendency to grow in **self-organised nanostructures**. By controlling crystal growth conditions, a variety of crystal shapes are possible. Researchers have been able to grow nanoscale wires, rods, rings, etc. (**Figure 21**). Zinc oxide nanocolumns are of particular interest since low-temperature photoluminescence measurements have revealed intense and detailed **ultraviolet light emission** near the optical band gap of ZnO at 3.37 eV. Thus, ZnO can act as an optical amplification medium and as a laser resonator.

Zinc oxide wires arrayed on a surface are also being investigated as piezoelectric elements for **miniaturised power sources**. This would allow the creation of flexible, portable power sources that could be included in textiles so that energy from body motion, light wind, air flow, etc., could be scavenged.

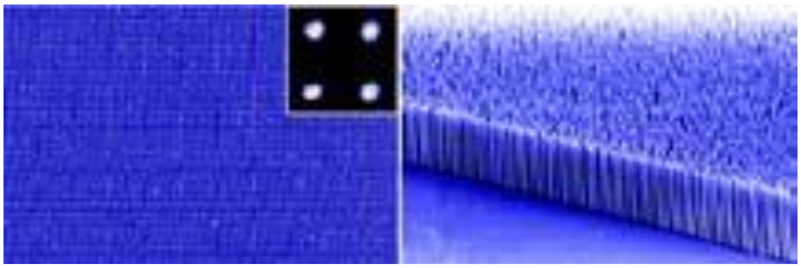

Figure 21: Patterned ZnO grown as vertical pillars in an arrayed format

Indium tin oxide

Indium tin oxide (ITO) is a semiconducting material whose main feature is the **combination of electrical conductivity and optical transparency**. ITO is typically around 90 % indium(III)-oxide (In_2O_3) and 10 % tin(V)-oxide (SnO_2). It is widely used in its thin-film form as transparent electrodes in liquid crystal displays, touch screens, LEDs, thin-film solar cells, semiconducting sensors, etc. ITO is an **infrared absorber** and is currently used as a thermal insulation coating on window glass. Its anti-static properties make it additionally useful in applications such as the packaging and storage of electronic equipment. Since the material is very expensive, alternative materials, such as fluorescent tin oxides and aluminium zinc oxides are being considered.

Reference:

• Luisa Filipponi and Duncan Sutherland, Nanotechnologies: Principles, Applications, Implications and Hands on Activities, Edited by the European Commission Directorate-General for Research and Innovation Industrial technologies (NMP) programme, 2013, Chapter 5.