

# Chapter 1

## Polymers

### 1.1 Atomic bonding

**Hybridisation** is the creation of new molecular orbitals from the overlap of core electron wavefunctions, and occurs when atoms in a molecule bond with each other. Most molecules are roughly 1D or 2D in nature, but not usually 3D like a crystal. Therefore most molecules bond across two dimensions.

#### 1.1.1 Molecular orbitals and Carbon

Let's consider carbon, depicted in [fig. 1.1](#). The hybridisation in carbon is called  $sp^2$  hybridisation. Take the ground-state of carbon: it has two electrons (up & down spins) in its  $1s$  shell, and 2 electrons in the  $1p_{x,y,z}$  shells.

When two carbons overlap, hybridisation occurs, creating a  $\pi$ . Because there is an overlap of two atomic orbitals, there are two resulting *molecular* orbitals. These are the bond and anti-bond, in this case  $\pi$  and  $\pi^*$ . The anti-bond has a much higher energy level than the bond, and consequently is usually unoccupied. However, this isn't the only wavefunction overlap that occurs in carbon, there is also the overlap of the  $sp^2$  orbitals which form the strong  $\sigma$  and  $\sigma^*$  bonds.

### 1.2 Polymer micro-structure and alignment

#### 1.2.1 Stacking

Polymer packing is complex, due to the variety of inclusions and degrees of freedom attainable in a film solution. This includes tie-chains and defects.

Typically, for well packed polymers with high degrees of orientation, stacking orientations are as follows:

- **backbone-stacking** is oriented along the direction of the backbone.
- **alkyl-stacking** is perpendicular to the backbone, but given the radial freedom of alkyl side-chains, this could be arranged in a variety of ways, or have little net uniformity.

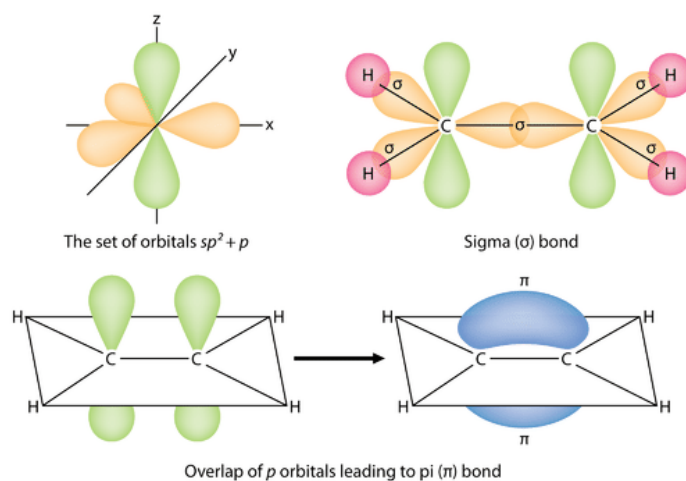


Figure 1.1: The description of various orbitals and their bonding, including the out-of-plane  $p_z$ -orbitals (green), the in-plane  $sp^2$ -orbitals (yellow) caused by the hybridisation of  $p_x, p_y, s$  orbitals. The emergence of bonding is also shown, with the overlap of in-plane  $sp^2$  orbitals (yellow) to form a strong  $\sigma$  bond, and with the overlap of  $p_z$ -orbitals (green) to form a  $\pi$  bond (blue) between atoms. Source: Zachary Wilson, CK-12 Foundation<sup>1</sup>.

- **$\pi$ -stacking** is perpendicular to the plane of the molecule, and is primarily related to the parallel alignment of backbones, though will be affected by alkyl behaviour as well.

Sometimes one type of stacking may exist without the presence of others.

### 1.2.2 Something

## 1.3 Solar Cells

Something else

# Bibliography

<sup>1</sup>Z. Wilson, *9.24: Sigma and Pi Bonds*, en, June 2016.

# Glossary

$\pi$  A chemical bond between two atoms, due to overlap in  $s$  and  $p$  orbitals. For example, in Carbon  $sp^2$  hybridisation creates  $\pi$  bonds. [1](#), [2](#)

**$\pi$ -stacking** Stacking in the out-of-plane direction, relative to the 2D molecular plane. The typical miller indices are assigned to the second index, i.e. (0,1,0). [2](#)

$\pi^*$  An anti-bond version of a  $\pi$  bond, due to overlap in  $s$  and  $p$  orbitals. A higher energy than that of the  $\pi$  bond. [1](#)

$\sigma$  A chemical bond between two atoms, due to overlap in  $p$  orbitals perpendicular to the atomic displacement. For example, in Carbon  $p^z$  overlap creates  $\sigma$  bonds. [1](#), [2](#)

$\sigma^*$  An anti-bond version of a  $\sigma$  bond, due to anti-bonding overlap in  $p$  orbitals perpendicular to the atomic displacement. A higher energy than that of the  $\sigma$  bond. [1](#)

**alkyl-stacking** Stacking in the direction of Alkyl side-chains, that is perpendicular to the backbone. [1](#)

**backbone-stacking** Stacking along (parallel to) the main chain direction of a polymer. [1](#)

**hybridisation** The overlap of atomic orbitals that creates bonding and anti-bonding, leading to lower energy (and higher energy) bonding states. [1](#)