

## 2002 PART IIB POLYMER COURSE

### MRMs Lecture notes

Note; These notes are not complete. Additional material is provided in the lecture.

#### 1. **Polymers Introduction**

- 1.1 Key Natural Polymers
- 1.2 Key Synthetic Polymers
- 1.3 The chemical and physical function of Polymers
- 1.4 Topological construction of polymer chains
  - 4.1 The chemistry of the repeat unit
  - 4.2 The chemical sequencing of the repeat unit
  - 4.3 Functionality
  - 4.4 Copolymers
  - 4.5 Blends
  - 4.6 Chain length
- 1.5 Characterisation of polymers

#### 1 **Polymers, Introduction**

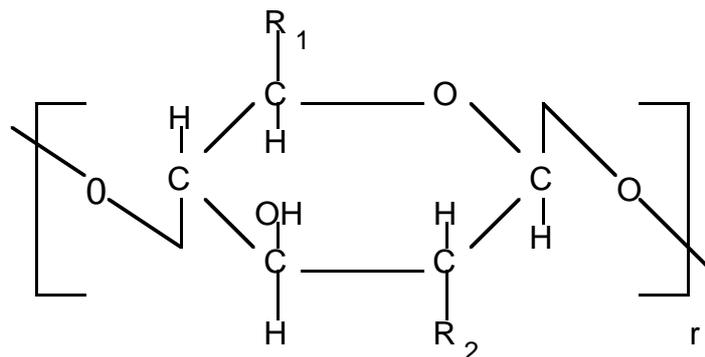
Polymers are all pervading both as natural and synthetic long chain molecules. Nearly all man made polymers play a structural role, although natural polymers contain vital chemical information, which of course forms the basis of life, DNA. Polymers also form enzyme chains that are capable of building fantastic structures such as the human body.

This course however concentrates on large tonnage synthetic polymers!

## 1.1 Key natural polymers

**Cellulose derivatives** A natural, structural polymer which also has a function as an energy source.

### Polysaccharide chain

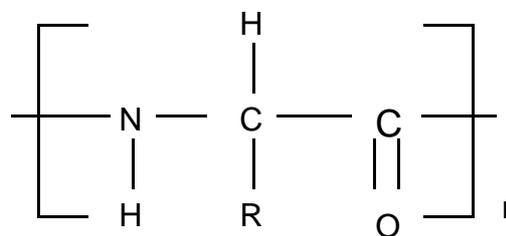


R<sub>1</sub> and R<sub>2</sub> are different alkyl groups

r = number of repeat units

Occurrence /function	Cellulose	.....
	Chitin	....., prawn shells!
	Starch	.....

**Proteins** A natural polymer that can have both structural and chemical function.



Polypeptide chain

R = Amino acid

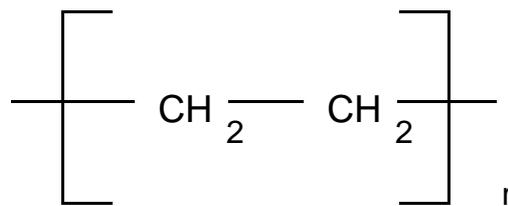
Ex R = H Glycine

Occurrence / function

Amino acid sequencing	DNA, RNA "Stuff of life"
Collagen	.....
Keratin	.....
Gelatin	animal extract, forms gels and jelly!

## 1.2 Key synthetic polymers

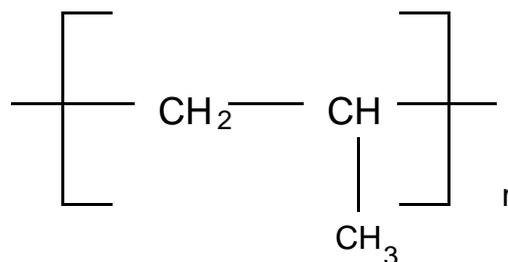
**Polyethylene (PE).** Sixty eight years since discovering (1933) now the largest world tonnage commodity polymer. Typical single plant 300,000 tonnes/annum. At least 200 plants of this size in the world.



$m_o$  = Molecular mass of repeat unit,  $m_o=28$  kg/kmol  
 $T_m$  = Melting temperature ~

## Polypropylene (PP)

A bulk commodity, addition polymerisation polymer discovered in 1956 with the discovery of Zeigler Natta catalysts.

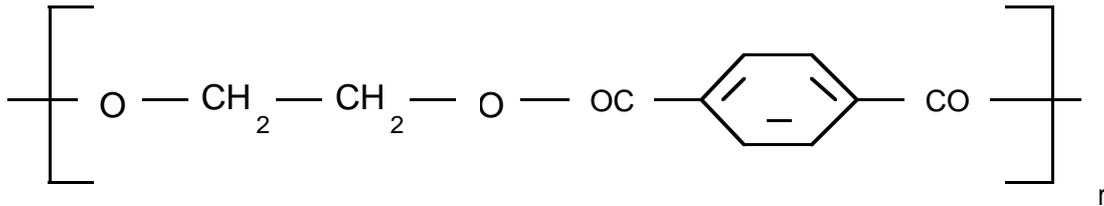


$m_o$  = 42 kg/kmol  $T_m \approx$

Function Similar to PE

## Polyethylene terephthalate (PET)

A bulk commodity, stepwise polymerisation thermoplastic.



$m_0 =$

$T_m \approx 230^\circ\text{C}$

Function

Fibres

"Terylene shirts", Dacron (Dupont)

Films

Dacron. ....

Blow moulding

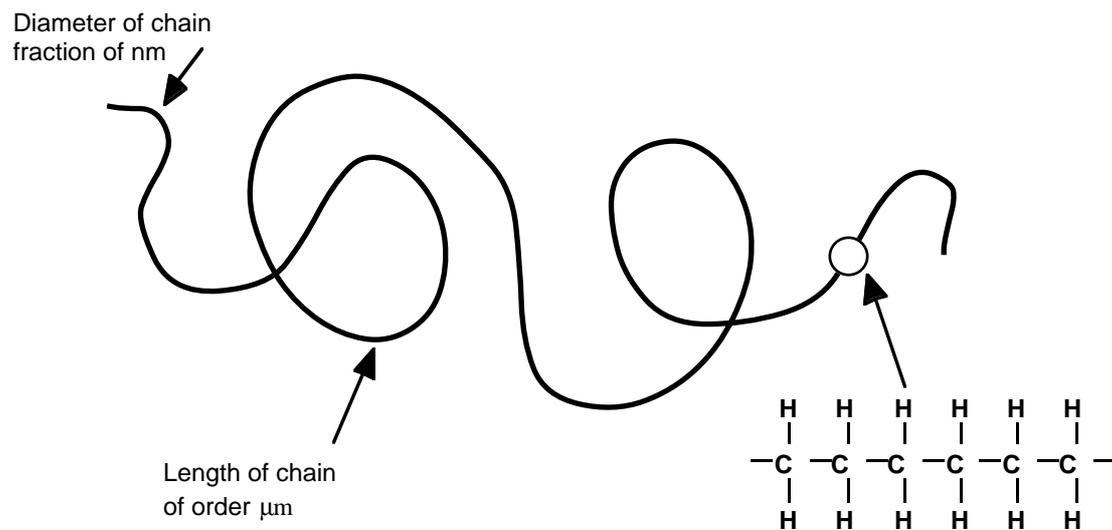
PET bottles

1980 0 tonnes/year

1996  $\sim 10^6$  tonnes/year

### 1.3 The chemical and physical function of polymers

Polymers can be constructed in many different ways and consequently there is greater richness and complexity in polymer systems than in smaller molecules. Certain features of polymers can depend on the specific chemistry of the repeat unit, whilst other properties are sensitive to chain length.



Some properties depend essentially only on chain length



Mechanical properties

Strength  
Toughness  
Stiffness



Viscosity and rheology

Some properties depend on the chemistry of chain



Mechanical properties

Glass transition temperature  $T_g$ ,  
Melting temperature  $T_m$   
Crystallinity



Chemical function

DNA  
Protein folding  
Polymer enzyme/catalytic action

### 1.3 Topological construction of polymer chains

There are many different ways in which a polymer chain can be constructed. This course deals almost entirely with linear chains, but you should be aware that there are other important possibilities.

The way in which the chain is built up can effect different properties. Both the chemist, the physicist and the chemical engineer can influence the final properties of the manufactured polymer. Here are some examples of how the different chemistry and topology of construction can alter polymer properties.

#### 1.4.1 The chemistry of the repeat unit

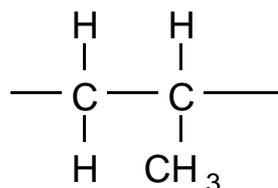
The fundamental choice of the chemical repeat unit can be crucial for many, but not all properties. Ethylene ( $\text{CH}_2 = \text{CH}_2$ ) produces PE which forms a semi crystalline polymer with a  $T_m$  of  $135^\circ\text{C}$ . Propylene ( $\text{CH}_2 = \text{C}_2\text{H}_5$ ) produces PP which again forms a semi crystalline polymer with a  $T_m$  of  $176^\circ\text{C}$ . The differences in  $T_m$  is due to the chemistry of the repeat units.

$T_m$  and  $T_g$  are sensitive to repeat unit chemistry.

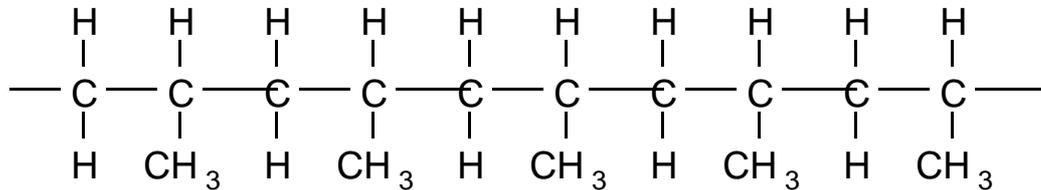
The chemistry and chemical sequence of natural polymers is crucial to most biological function.

#### 1.4.2 The chemical sequencing of the repeat unit

Sequencing  $\equiv$  tacticity, Consider for example polypropylene

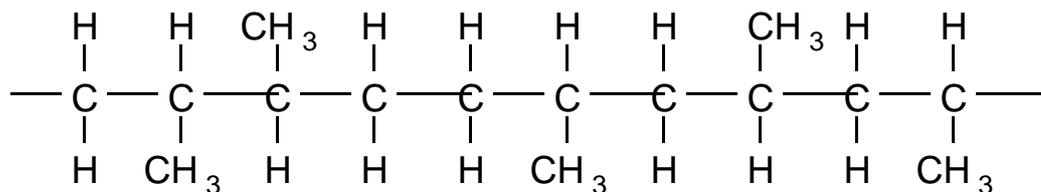


The molecule could form a regular isotactic chain by coupling in a regular way



If this happens the chain is highly ordered and more likely to crystallise.

Alternatively the chain may form to produce an irregular atactic chain.

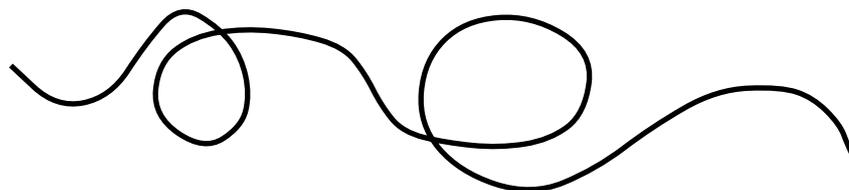


This less regular chain is less likely to fall into crystallographic register and will probably be amorphous in the solid state.

### 1.4.3 Functionality

The functionality of a monomer or chain relates to the number of reactive groups present. Generally, in order to form a linear of chain, you need ..... functional (reactive) groups/monomer. In some cases additional functionality may be present and you can form branched or network polymers. Functionality and chemical structure can have a profound affect on the final product.

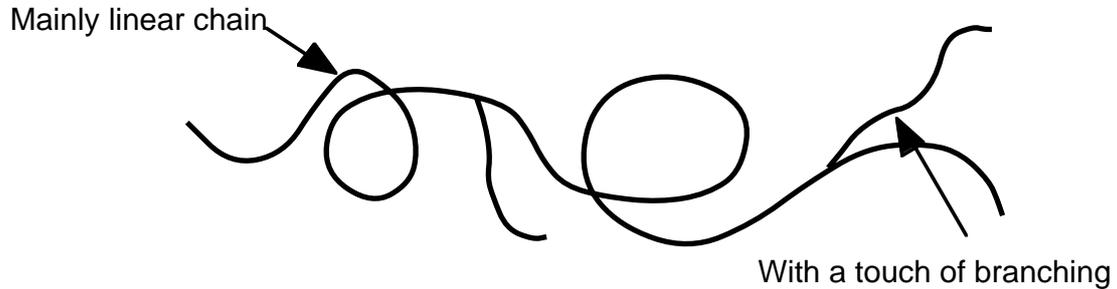
"..... functional groups"  $\Rightarrow$  Linear chains



Linear chain polymer, normally melt and therefore can be melt

processed and polymerised.

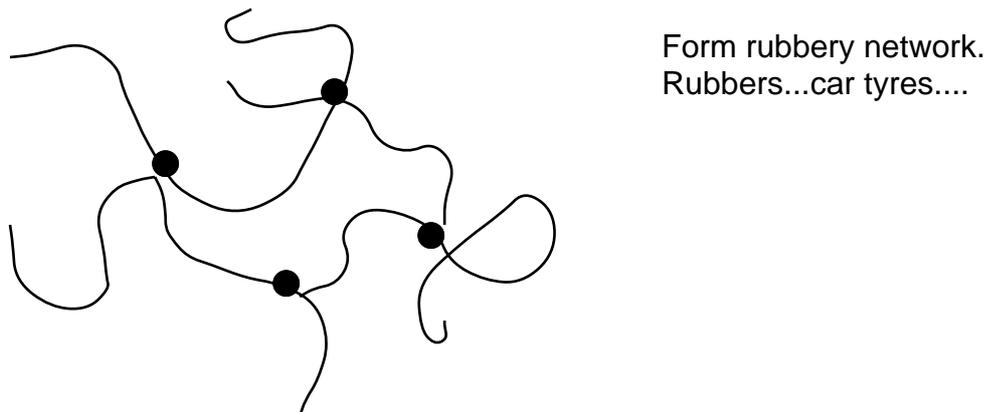
"A dash of ...functional groups"  $\Rightarrow$  Long chain branching



Branched polymers, such as low density polyethylene (LDPE) can have improved processibility and toughness.

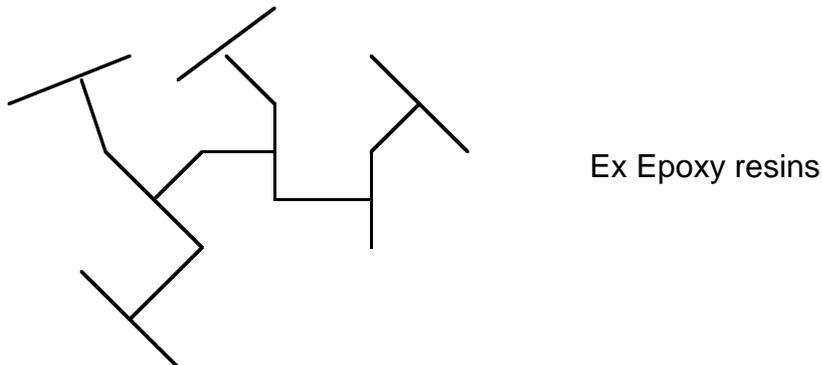
"Network polymers"

Linear chains with additional crosslinkers.



Trifunctional monomers

These types of monomers form a three dimensional network which when formed is unprocessable at elevated temperature - thermostat resins.



## 1.4.4 Copolymers

Copolymerisation is extensively used now for both speciality and commodity polymers. Di-block copolymers are polymers that are formed from two different repeat units such as A [CH<sub>2</sub> - CH<sub>2</sub>] and B [CH<sub>2</sub> - CH]. The resulting polymer consists of A - B chains  
CH<sub>3</sub>

A-A-A-A-A-A-A-B-B-B-B-B-B

Tri-block copolymers are receiving a lot of current attention, as they have the potential to form clever "nanostructures". An example could be ethylene A [CH<sub>2</sub> - CH<sub>2</sub>] which is hydrophobic and ethylene oxide B [CH<sub>2</sub> - CH<sub>2</sub> - O] which is hydrophilic.

A-A-A-A-A-B-B-B-B-B-B-A-A-A-A

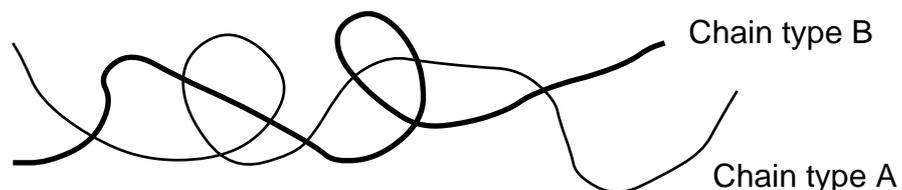
These types of polymers can phase separate to form interesting microstructures.

Random copolymers form where the chain has "random" sequencing of two repeat units alongside the chain.

..... A-B-A-A-B-A-A-A-B-B-A-B .....

## 1.4.5 Polymer blends

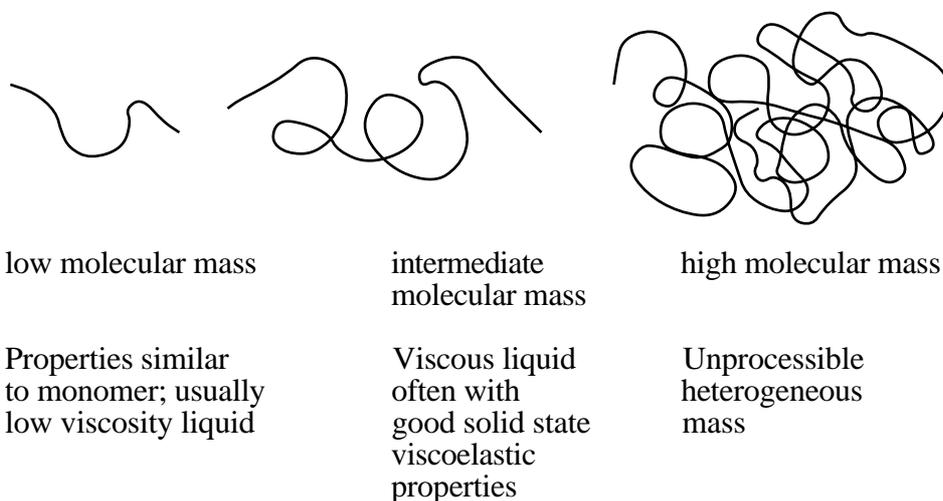
The blending of different polymer chains is extensively carried out. Here two or more polymer types are physical blended together either by intense mixing within the melt or via solution processing.



The chains may or may not form a miscible blend.

## 1.4.6 Chain length

A very important feature of any commercially produced polymer is the chain length of the molecule. This controls many properties including viscosity, processibility, mechanical and structural properties. The chain length can also have minor effects on  $T_g$  and  $T_m$ . For a given monomer chemistry, chain length is the key additional factor that has to be taken into account



Polymers typically have a molecular mass between -  $10^3$  -  $10^7$  kg/kmol. Most commercial polymers have a molecular mass distribution (MMD). See Section 2.

## 1.5 Characterisation of polymers

Commercially and of course scientifically it is very important to know what you have made. Knowledge of the monomer usually, but not always, gives a clear idea of the chemical structure of the chain.

Standard chemical techniques used to identify the "chemistry" of the chain including  
NMR, spectroscopy

IR, "

X-ray diffraction

Other less standard techniques are used to determine the "physical" state of the polymer.

Melting behaviour DSC differential scanning calorimetry

Mechanical behaviour DMTA differential mechanical thermal analysis

Density An old and rather poor method used for ranking different grades of the same polymer.

High density PE HDPE

Low density PE LDPE

Density is a measure of % crystallinity

Melt flow index (MFI) A one parameter viscosity measurement that gives an indication of molecular mass. Still extensively used.

The MFI of a polymer is the time taken for x grams of polymer to flow through a die of specification y when subject to a load of magnitude z.

High MFI = low molecular mass

Low MFI = high molecular mass

Viscosity ( $\eta$ ) The viscosity of a polymer melt is very sensitive to mm of chain m where  $m = m_0 \times r$

$$\eta \propto m^{3.4}$$

If  $\eta = 10^{-2}$  Pas for  $m = 10^4$  what is  $\eta = (6.3 \times 10^{-4}$  Pas) for  $M = 10^6$ .

There are complications because  $\eta$  is Non Newtonian.

### **Molecular mass distribution MMD**

Measurement of MMD and characterisation from this is currently the most extensive and powerful way of characterising commercial and biopolymer chains.

## **Check list.**

Linear polymer chains. What are the key factors?

What factor controls processing and mechanical properties?

$T_g$ ,  $T_m$  What are they? And what aspect of the polymer controls their values?

Why are polymers so incredibly important?