**3.12. Polymers**

There are two types of polymerisation: **addition** and **condensation**

**Addition Polymerisation**

An addition polymer forms when unsaturated monomers react to form a polymer.

Monomers contain C=C bonds. Poly(alkenes) are chemically inert due to the strong C-C and C-H bonds and non-polar nature of the bonds and therefore are non-biodegradable.

Chain forms when same basic unit is repeated over and over.

You should be able to draw the polymer repeating unit for any alkene. For but-2-ene:

\[
\begin{align*}
H_2C-CH=CH-CH_3 & \rightarrow \quad \text{It is best to first draw out the monomer with groups of atoms arranged around the double bond.}
\end{align*}
\]

**Condensation Polymerisation**

The two most common types of condensation polymers are **polyster**s and **polyamides** which involve the formation of an ester linkage or an amide linkage.

In condensation polymerisation there are two different monomers that add together and a small molecule is usually given off as a side-product e.g. H₂O or HCl.

The monomers usually have the same functional group on both ends of the molecule e.g. di-amine, di carboxylic acid, diol, diacyl chloride.

Forming polyesters and polyamide uses these reactions we met earlier in the course:

- Carboxylic Acid + Alcohol \( \rightarrow \) Ester + water
- Acyl chloride + Alcohol \( \rightarrow \) Ester + HCl
- Carboxylic Acid + Amine \( \rightarrow \) amide + water
- Acyl chloride + Amine \( \rightarrow \) amide + HCl

If we have the same functional group on each end of molecule we can make polymers so we have the analogous equations:

- dicarboxylic acid + diol \( \rightarrow \) poly(ester) + water
- diacyl dichloride + diol \( \rightarrow \) poly(ester) + HCl
- dicarboxylic acid + diamine \( \rightarrow \) poly(amide) + water
- diacyl dichloride + diamine \( \rightarrow \) poly(amide) + HCl

Using the carboxylic acid, to make the ester or amide would need an acid catalyst and would only give an equilibrium mixture. The more reactive acyl chloride goes to completion and does not need a catalyst but does produce hazardous HCl fumes.

**Terylene - a common polyester**

\[
\begin{align*}
{\text{Benzene-1,4-dicarboxylic acid}} & \quad + \quad n \quad {\text{Ethane-1,2-diol}} \\
{\text{HO}} & \quad + \quad {\text{OH}} & \quad \rightarrow & \quad \text{Polyester} & \quad + \quad 2n-1 \quad \text{H}_2\text{O}
\end{align*}
\]

Terylene fabric is used in clothing, tire cords.

\[
\begin{align*}
\text{Pentanedioyl dichloride} & \quad + \quad n \quad {\text{Benzene-1,4-diol}} \\
{\text{Cl}} & \quad + \quad {\text{OH}} & \quad \rightarrow & \quad \text{Polyamide} & \quad + \quad 2n-1 \quad \text{HCl}
\end{align*}
\]

The -1 here is because at each end of the chain the H and OH are still present.

N Goalby chemrevise.org
Nylon 6,6 - a common polyamide

\[
n \text{HO}_2C-(CH_2)_4-CO_2OH + n \text{H}_2N-(CH_2)_6-N\text{H}_2 \rightarrow \left[ \begin{array}{c} \text{C} \text{O} \\ \text{N}-(CH_2)_6-N\text{H} \end{array} \right]_n + 2n-1 \text{H}_2\text{O}
\]

The 6,6 stands for 6 carbons in each of the monomers. Different length carbon chains produce different polyamides.

Kevlar - a common polyamide

\[
n \text{HO}_2C-C_{\text{phen}}-\text{CO}_2H + n \text{H}_2N-\text{C}_{\text{phen}}-\text{NH}_2 \rightarrow \left[ \begin{array}{c} \text{N} \\ \text{NH} \end{array} \right]_n + 2n-1 \text{H}_2\text{O}
\]

Note on classification for condensation polymers

If asked for type of polymer: It is polyamide or polyester
Whereas type of polymerisation is condensation

It is also possible for polyamides and polyesters to form from one monomer, if that monomer contains both the functional groups needed to react.

4-hydroxybutanoyl chloride

\[
\text{HO}-(CH_2)_3-\text{C} \quad \rightarrow \quad \text{O}-(CH_2)_3-\text{C}=\text{O}-(CH_2)_3-\text{C}=\text{O}
\]

3 repeating units

2-hydroxyproanoic acid (lactic acid)

\[
\text{HO}-\text{CH}-(\text{CH}_3)\text{C} \quad \rightarrow \quad \text{CH}_3-\text{C}=\text{O}-(\text{CH}_3)-\text{C}=\text{O}-(\text{CH}_3)-\text{C}=\text{O}
\]

3 repeating units poly(lactic acid)

2 lactic acid molecules can also form a ring diester

4-hydroxypentanoic acid

\[
\text{O}-\text{CH}-(\text{CH}_3)\text{C} \quad \rightarrow \quad \text{O}-(\text{CH}_3)\text{C}=\text{O}-(\text{CH}_3)-\text{C}=\text{O}-(\text{CH}_3)-\text{C}=\text{O}
\]

1 repeating unit

It is possible for some of these compounds to form various cyclic esters under different conditions from forming the polymer.
You do not need to learn these but may be asked to deduce structures from information given.
Disposal of Polymers

Landfill
The most common method of disposal of waste in UK. Many are now reaching capacity.
European regulations will mean councils are charged much more for using landfill.
Most polymers (polyalkenes) are non-biodegradable and take many years to break down.
Could use more biodegradable plastics, e.g. Polyamides and cellulose and starch based polymers to improve rates of decomposition

Incineration
Rubbish is burnt and energy produced is used to generate electricity.
Some toxins can be released on incineration. Modern incinerators can burn more efficiently and most toxins and pollutants can be removed. Greenhouse gases will still be emitted though.

Volume of rubbish is greatly reduced.

Recycling
Saves raw materials - nearly all polymers are formed from compounds sourced/produced from crude oil. Saves precious resources.
Polymer need collecting/sorting - expensive process in terms of energy and manpower.
Polymer can only be recycled into the same type - so careful separation needs to be done.
Thermoplastic polymers can be melted down and reshaped.

Chemical reactivity of condensation polymers
Polyesters and polyamides can be broken down by hydrolysis and are, therefore, biodegradable

The reactivity can be explained by the presence of polar bonds which can attract attacking species such as nucleophiles and acids

Hydrolysis
Polyesters and polyamides can be hydrolysed by acid and alkali
The hydrolysis will result in the original monomers forming - although the carboxylic acid or amine group will be in salt form depending on whether the conditions are alkaline or acidic

\[
\text{-CO(CH}_2\text{)_4CONHC(CH}_3\text{)}_2\text{CH}_2\text{O-} \xrightarrow{\text{HCl}} \text{HO-CH}_2\text{CH}_2\text{COOH} + \text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+
\]

\[
\text{-CO(CH}_2\text{)_4CONHC(CH}_3\text{)}_2\text{CH}_2\text{O-} \xrightarrow{\text{NaOH}} \text{OCH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{NCH}_2\text{OH}
\]

This polymer has both an amide and ester link

Intermolecular bonding between condensation polymers chains
Polyesters have permanent dipole bonding between the C\(\delta^+\)=O\(\delta^-\) groups in the different chains in addition to the van der waals forces between the chains.

Polyamides (and proteins) have hydrogen bonding between the oxygen in C\(\delta^+\)=O\(\delta^-\) groups and the H in the N\(\delta^-\)--H\(\delta^+\) groups in the different chains in addition to the van der waals forces.
Polyamides will therefore have higher melting points than polyesters.