



University of
South Australia

ENR116 Engineering Materials

Module 4 Non-metals and Corrosion

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Welcome to ENR116, Engineering materials. This lecture summary is part of Module 4, non metals and corrosion



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ENR116 – Mod. 4- Slide No. 2

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Polymer chemistry

Polymer chemistry



Intended Learning Outcomes

At the end of this section, students will be able to:-

- Identify the general **structural characteristics** of polymers.
- Understand how these structures are **chemically characterised**.

At the end of this lecture you should be able to identify the general **structural characteristics** of polymers and understand how these structures are **chemically characterised**.

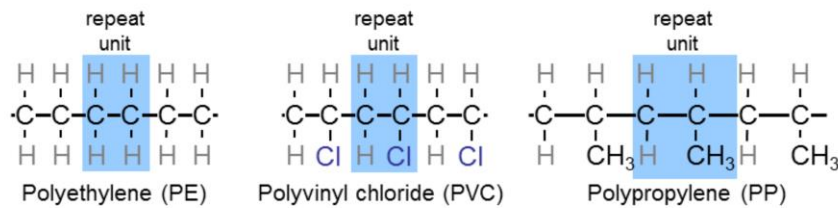


Polymers



What is a polymer?

Poly **mer**
many repeat unit



Adapted from Fig. 14.2, Callister & Rethwisch 8e.

So, what is a polymer? The word polymer comes from the Greek poly, meaning many, and mer, meaning unit. So a polymer is a structure made of many repeating units. We can see that in the examples shown here. Polyethylene has a simple repeat unit of C_2H_4 . Polyvinyl chloride, has a repeat unit, or monomer, of $\text{C}_2\text{H}_3\text{Cl}$. Polypropylene is made of many repeating $\text{C}_2\text{H}_3\text{CH}_3$ units.



Natural polymers

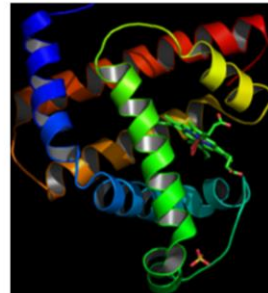
Wood – composed of cellulose fibres and lignin.



Proteins - composed of a various amino acids which are bonded together via covalent peptide bonds.



Natural rubber:
Latex from the
Para rubber tree



There are many naturally occurring polymers. Wood is a good example. Wood is actually a composite, composed of cellulose fibres and lignin. Paper and cotton are nearly pure cellulose.

Another example of a natural polymer is a protein. Proteins are composed of various amino acids which are bonded together via covalent peptide or amide bonds. Proteins have extremely complicated 3D structures. Wood, silk and leather are all examples of naturally occurring protein based polymers.

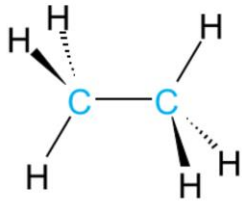
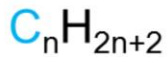
The final natural polymer that we will highlight here is natural rubber. Natural rubber is latex from the para rubber tree, and is actually an emulsion consisting of proteins, alkaloids, starches, sugars, oils, tannins and resins, as well as the naturally occurring polyisoprene.



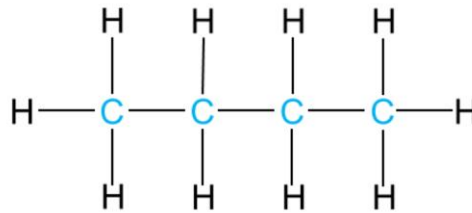
Polymer composition

Most polymers are hydrocarbons i.e. made up of H and C.

Saturated hydrocarbons (alkanes, paraffin compounds) - each carbon bonded to four other atoms.



Ethane



Butane

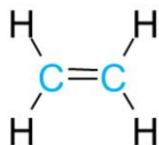
The vast majority of polymers are hydrocarbons, that is, they are composed of hydrogen and carbon. Saturated **hydrocarbons**, such as alkanes and paraffin compounds, contain carbon covalently bonded to four other atoms. These compounds have the general formula $\text{C}_n\text{H}_{2n+2}$. Two examples of saturated hydrocarbons are ethane and butane.



Unsaturated hydrocarbons

- Contain double and/or triple bonds.
- Relatively reactive - can form new bonds.

Double bond (alkenes) - ethylene or ethene - C_nH_{2n}



Triple bond (alkynes) - acetylene or ethyne - C_nH_{2n-2}



Unsaturated - carbon is not bonded to four other atoms.

Unsaturated hydrocarbons contain double and or triple bonds. As the carbon in these structures is not already bonded to the maximum four other atoms, unsaturated hydrocarbons are relatively reactive and can readily form new bonds.


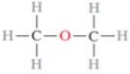
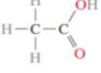



Carbon chains that contain a double bond form the alkenes, and have the general formula C_nH_{2n} . You can see the structure of ethene here. Hydrocarbons with a triple bond in the chain form alkynes, and these have the general formula C_nH_{2n-2} . This is ethyne.

So, to summarise, in a saturated hydrocarbon, carbon is bonded to four other atoms, whereas in the unsaturated hydrocarbons, carbon is bonded to fewer than the maximum four other atoms.



Common polymer classes (groups)

Table 14.2 Some Common Hydrocarbon Groups

Family	Characteristic Unit	Representative Compound
Alcohols	$R-OH$	 Methyl alcohol
Ethers	$R-O-R'$	 Dimethyl ether
Acids	$R-C(=O)OH$	 Acetic acid
Aldehydes	$R-C(=O)H$	 Formaldehyde
Aromatic hydrocarbons	  Phenol	

R and R' represent organic groups such as CH_3 , C_2H_5 , and C_6H_5 (methyl, ethyl, and phenyl).

*The simplified structure  denotes a phenyl group.

Here are some of the common functional groups that can be found on a hydrocarbon chain. The nature of the functional groups in a polymer grant it unique physical and chemical properties.

The alcohol groups comprise a carbon bonded to an oxygen and a hydrogen, whilst the acids have a carbon double bonded to oxygen, in addition to an OH group.

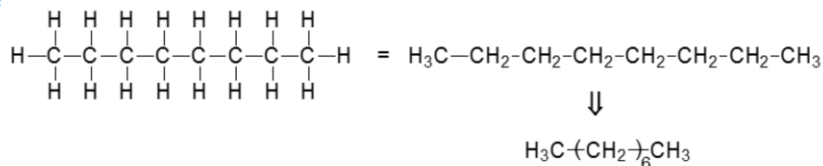
The aromatic hydrocarbons are interesting. The simplified hexagonal structure here represents a six carbon ring, which is depicted as containing alternating single and double carbon bonds. However, these electrons would more accurately be considered as being delocalised within the cyclic structure.



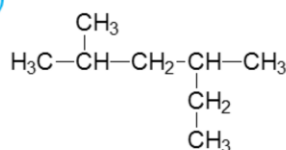
Isomerism

Isomerism: Two compounds with same chemical composition can have quite different structures, Example C_8H_{18}

n-octane



2-methyl-4-ethyl pentane (isooctane)



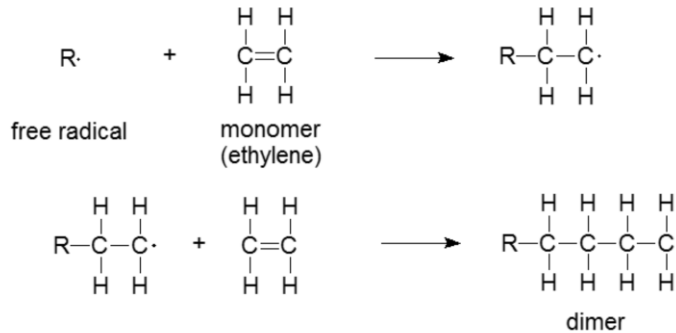
It's possible to have a situation where two compounds have identical chemical compositions, but different structures. This is a phenomenon known as isomerism. An example of this is octane, which has the nominal formula C_8H_{18} .

The first structure shown here is for the fully saturated, linear hydrocarbon form of octane (called n-octane). However, here you can see the structure for 2-methyl-4-ethyl pentane, or isooctane, which also has eight carbons and 18 hydrogens, but clearly a very different structure to the linear example. Note that in this case, it isn't possible to switch from one isomer to another without breaking and reforming bonds. Later in this lecture summary we'll return to look at some specific forms of isomerism.

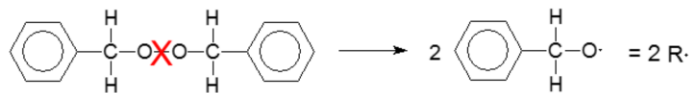


Synthesis of polymers

Free radical polymerization:



Initiator: Example - benzoyl peroxide



Now we've looked at some of the basic features of polymers, we're now going to take a look at how polymers are synthesised. We are going to address two different methods for generating polymers; namely free radical (or addition) polymerization and polycondensation (or step) polymerization.

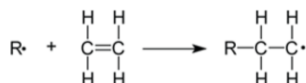
Many polymers are synthesized via free radical polymerization. Here a free radical, represented by R dot, will attack the double bond of a monomer species. This effectively breaks open the double bond, and creates a new radical. This free radical is highly reactive and will go on to attack another monomer, which in turn will form a dimer, trimer and so on. The initiator that creates the free radical has to be a particular kind of molecule. In the example here, benzoyl peroxide, the structure includes contains a single O-O bond. This bond is relatively weak and will cleave easily, generating two free radicals.



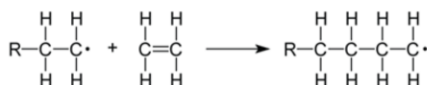
Addition (radical) polymerization

Radical polymerization is used in the synthesis of polyethylene, polypropylene, poly(vinyl chloride), and polystyrene, as well as many of the copolymers.

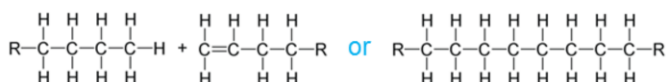
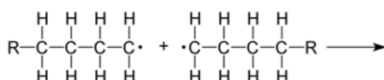
Initiation:



Propagation:



Termination:



Disproportionation

Combination

Addition polymerization utilizes free radicals in order to form long polymer chains. The process is classically split into three stages - initiation, propagation and termination. The initiation stage describes the process of the free radical, R, reacting with an unsaturated molecule such as ethylene, as shown here. This forms a new radical with the free electron on the carbon atom of the ethylene.

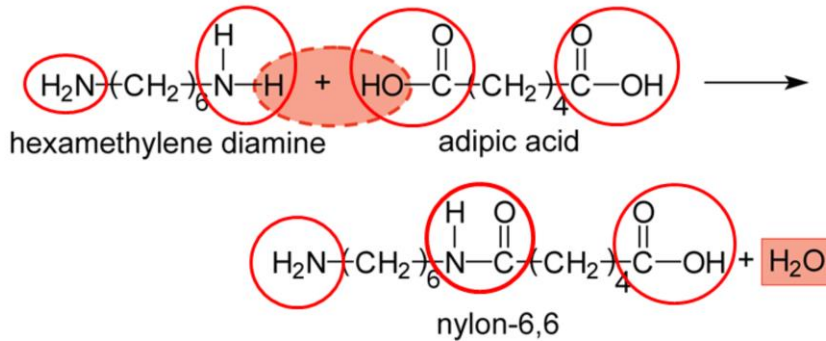
During propagation, the monomer units will keep adding to this growing chain, as shown here. This addition can happen hundreds and thousands of times before the reaction is terminated.

Termination usually occurs in one of two ways. Termination by disproportionation, or termination by combination. In termination by disproportionation, you finish with two molecules, one a fully saturated polymer and the other containing an unsaturated component. In termination by combination, two radicals combine and you end with a single, fully saturated polymer chain.



Polycondensation (step) polymerization

Monomers containing functional groups



Polycondensation, or step, polymerization, is used predominantly for monomers containing functional groups. In the example here, two molecules are undergoing an esterification reaction. This is typically a reaction between an amine and an acid. In the example here you can see here hexamethylene diamine and adipic acid reacting to form Nylon 6,6. Note that both molecules are bifunctional, that is, they each have two functional groups. Two amines in the case of the diamine, and two acid centres in adipic acid.

In the course of the esterification reaction, water is eliminated, generating a new molecule with a central amide bond, but also still two unreacted functional groups, at either end of the molecule. Because it has these unreacted groups, this new molecule can itself go on and react again and again, creating extensive polymer chains.



Polymer molecules

Homopolymer – composed of the same repeat unit.

Some basic polymer definitions. Up to this point, we have assumed that polymers are made entirely of the same repeat units, but in fact this is only true for a class of polymers known as homopolymers.

A co-polymer is composed of two or more different repeat units.

Functionality is the number of bonds that the starting monomer can form, and as such will dictate the structure of the final polymer


Bifunctional monomers, such as the hexamethylene diamine and adipic acid in the previous slide, generate linear polymers.

Trifunctional monomers give rise to highly crosslinked, networked 3 dimensional polymers.



Bulk or commodity polymers

Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer	Repeat Unit
 Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array}$

So let's have a brief look at some of the most common polymer repeat units, and their applications.

Polyethylene is a simple hydrocarbon with the basic repeat unit C_2H_4 , as shown here.

Poly(vinyl chloride) is a familiar component of PVC pipes, and it has a similar repeat unit but with a single chlorine in place of one of the hydrogen atoms.

PTFE has a completely fluorinated carbon backbone. PTFE is used extensively in high temperature applications, such as frying pans, or electrical wiring.

The last example here, polypropylene, contains a methyl group in place of one of the hydrogen atoms. Polypropylene is used in similar applications to polyethylene, such as packing and textiles. Uniquely in Australia, polypropylene is also found in banknotes!



Bulk or commodity polymers

Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer	Repeat Unit
 Polystyrene (PS)	

The monomers in this slide are slightly more complex than the previous examples.


Polystyrene, PS, contains a benzene ring functional group, whilst polymethyl methacrylate or, PMMA, has both a methyl group and ester functionality. PMMA has excellent optical properties and is used extensively in Perspex windows and similar applications. Polystyrene has applications in packaging, disposable tableware, pen casings and similar situations where a lightweight, economical plastic is required.

Bakelite, or phenol formaldehyde, is the first example we've had of a thermoset. Thermosetting polymers arise when the monomer species has a number of different reactive groups, resulting in the formation of a networked rather than a linear polymer. We'll talk more about networked polymers towards the end of this summary. Bakelite is extremely heat resistant, and as one of the first synthetic polymers, was a popular choice in the 1920s / 1930s for radio and telephone casing, kitchenware and toys.



Bulk or commodity polymers

Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer	Repeat Unit
 Poly(hexamethylene adipamide) (nylon 6,6)	$ \begin{array}{c} \text{H} \\ \\ -\text{N}-\left[\text{C} \right]_6-\text{N}-\overset{\text{O}}{\parallel}-\left[\text{C} \right]_4-\overset{\text{O}}{\parallel}- \\ \qquad \qquad \qquad \\ \text{H} \qquad \text{H} \qquad \text{H} \qquad \text{H} \end{array} $

A last few examples. We've already come across Nylon 6,6 in the discussion of step polymerization. This polyamide is often used in fibres for textiles and carpets, and even car airbags.

PET, poly(ethylene terephthalate) is used in the manufacture of disposable fizzy drink bottles, and even some textiles.

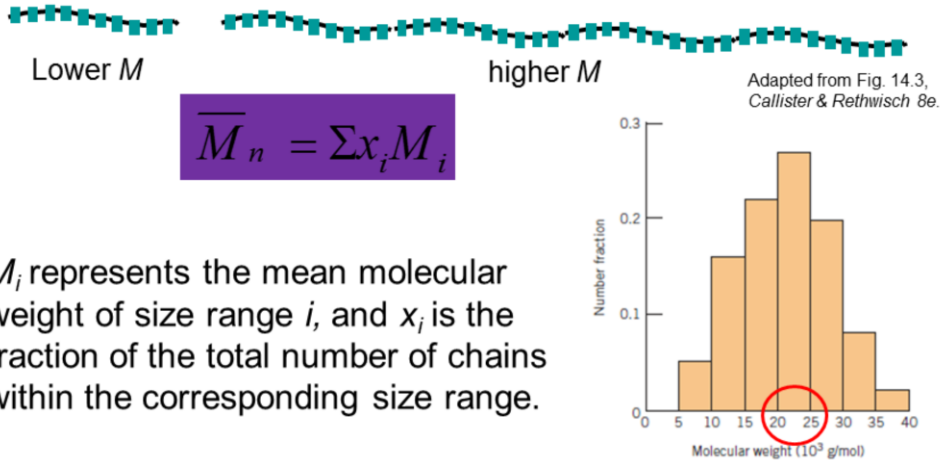
Polycarbonate is an advanced engineering plastic, with high impact resistance. It's used extensively in the automotive industry.

Note that all of the polymers here have very large and complex repeat units, and are therefore structurally quite different to the materials we looked at in the previous two slides.



Molecular weight

Number-Average molecular weight: Obtained by dividing the chains into a series of size ranges and then determining the number fraction of chains within each size range.



So, polymers are very large molecules and as such can have extremely large molecular weights. However, during the process of polymerization chains of different molecular weight are produced – because not all chains will grow to the same length, and therefore the final product will consist of a distribution of molecular weights. For this reason, we usually specify an average molecular weight for polymers.

There are two main ways by which we can define the average molecular weight of a polymer. These are by calculating the number average molecular weight, or the weight average molecular weight. We'll take a look at the number average method first.

The number average molecular weight is obtained by dividing the chains into a series of size ranges and then determining the number fraction of chains within each size range. **Here you can see a bar chart of this process, where the number fraction of the polymer chains has been plotted against each size range. You can see that in this case, the distribution is centered around the 20 to 25 x 10³ g per mole size range.**

Mathematically, this treatment is expressed as $\sum x_i M_i$

– basically, the number average molecular weight is the mean (middle) molecular weight of a size range, I , multiplied by the fraction of chains within that range.



Number average molecular weight

Example

N_i	M_i	x_i	Mix_i	
Mass Range	Mean Mass			
8,000-16,000	12000	0.05	600	Mean mass of range
16,000-24,000	20000	0.16	3200	
24,000-32,000	28000	0.24	6720	
32,000-40,000	36000	0.28	10080	
40,000-48,000	44000	0.2	8800	
48,000-56,000	52000	0.07	3640	Mean mass, multiplied by number fraction
		M_n		
		33,040		

$$\bar{M}_n = \sum x_i M_i$$

Lets go through a simple example of how to calculate the number average molecular weight.

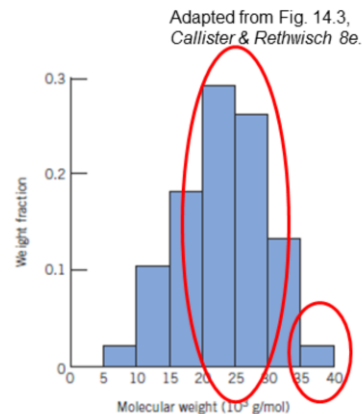


Molecular weight

Weight-Average Molecular weight: Is based on the weight fraction of molecules within the various size ranges.

$$\overline{M}_w = \sum w_i M_i$$

M_i represents the mean molecular weight of size range i , and w_i denotes the weight fraction of molecules within the same size interval.



The weight average molecular weight uses the weight fraction of the molecules rather than the number average, and how these fall into the size ranges. Here we can see a bar chart distribution for the same data set as before, but this time with the weight fraction contribution for each molecular weight range. The distribution is less symmetrical than before, and we can see that molecules in the 20 to 30 x 10³ g per mole weight range contribute most to the overall mass of the sample, together making up almost 60% of the total mass, a weight fraction of almost 0.6. Despite having a higher molecular mass individually, the longest polymer chains are responsible for a weight fraction of just 0.025 of the overall mass.

The mathematical expression for the weight average molecular weight is given as \overline{M}_w equals the sum of w_i times M_i , where w_i is the weight fraction of molecules in each group, and M_i is the mean, middle, molecular weight of each size interval.



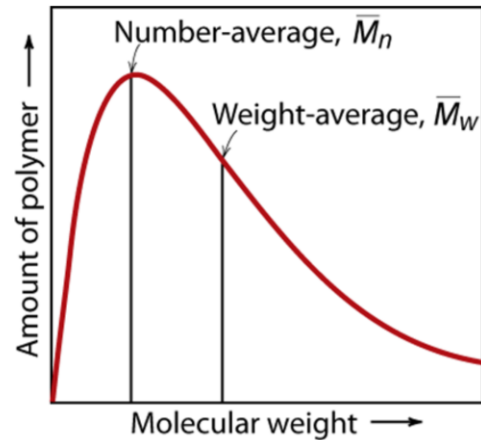
Molecular weight

Distribution of molecular weights for a typical polymer.

M_w is more sensitive to higher molecular weights.

$$PDI = \frac{M_w}{M_n}$$

Close to 1 – little variation in chain length across sample



Adapted from Fig. 14.4, Callister & Rethwisch 8e.

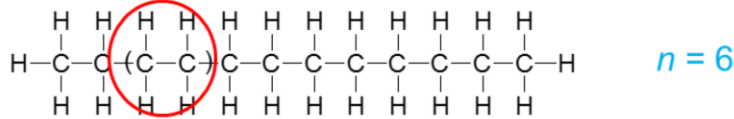
The number average and the weight average molecular weights are not necessarily the same. The weight average molecular weight is typically more sensitive to higher molecular weights, and is therefore the best choice for larger molecules. The number average weight is frequently used in the case of relatively small, simple polymer chains.

The distribution of molecular weights in a polymer sample can also be described by the ratio of the weight average molecular weight to the number average molecular weight, M_w over M_n . This ratio is the Polydispersity Index, or PDI. The closer the PDI is to 1, the more uniform the chain lengths within the sample.



Degree of polymerization, n

n = number of repeat units per chain



$$DP = n = \frac{\overline{M}_n}{m} \quad m - \text{the molecular weight of a repeat unit in a chain}$$

With increasing M_n melting temperature increases:

Up to 100 g/mol – liquid

Up to 1000 g/mol – wax

Above 1000 g/mol – solid

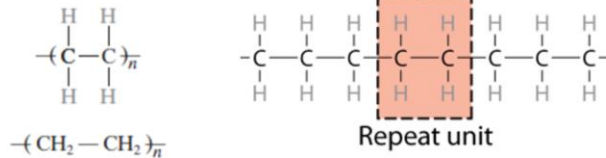
As a last method for describing the average chain size of a polymer, we'll introduce the degree of polymerisation, which is a measure of the average number of repeat units per chain. In the example here, the repeat unit is C_2H_4 , and there are six in the chain. The degree of polymerisation is calculated as the number average molecular weight, divided by the molecular weight of an individual repeat unit.

The molecular mass of a polymer has quite an impact on the final form of the material. Generally, as the average mass of the polymer chain increases, the melting temperature also increases. Polymers up to about 100 g / mol tend to be liquids, whilst those between 100 and 1000 g per mole are waxy type materials. Molecular masses greater than 1000 g per mole are solids. The vast majority of polymer materials fall into this last category.

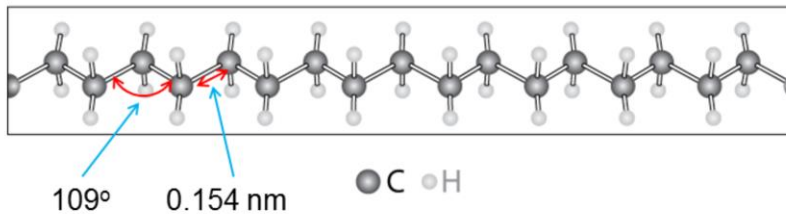


Molecular shape

polyethylene



Adapted from Fig.
14.1, Callister &
Rethwisch 8e.



Now that we've looked at how the molecular weight of a polymer is determined, we're going to change focus. For the last part of this lecture summary, we'll be discussing various aspects of the physical form of polymer chains.

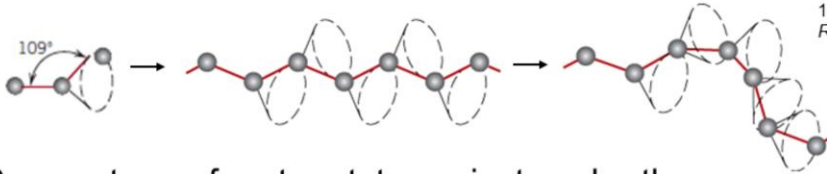
So, up until now, we've really considered polymers as two dimensional objects, with a rigid 90 degree angle between the C-C and C-H bonds. However, in reality this is not the case. This illustration, here, is a better representation of how a simple polymer is arranged in space, with a 109 degree angle between the C-C bonds, and a nominal bond length of 0.154 nm. However, even within this simple structure, segments can rotate or bend. This is the subject of our next slide.



Molecular shape

Conformation: Molecular orientation can be changed by rotation around the bonds. Note: no bond breaking is needed.

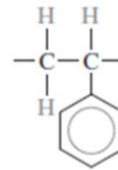
Adapted from Fig.
14.5, Callister &
Rethwisch 8e.



Segments are free to rotate against each other.

The degree of rotation depends on both the chemistry and repeat unit structure.

C=C makes segment rigid.



Bulky or side groups also restrict mobility.

Polymer conformation describes how the molecular orientation of a chain can be changed by rotation around the bonds. We don't need to make or break any bonds in order to do this. If you consider the saturated hydrocarbon shown here, you can see that each of the individual segments can rotate about their own C-C bond, changing the physical shape of the chain. The actual degree of rotation depends on the temperature of the system, and the chemistry and nature of the repeat unit structure.

Carbon carbon double bonds are effectively rigid, and prevent rotation within a segment.

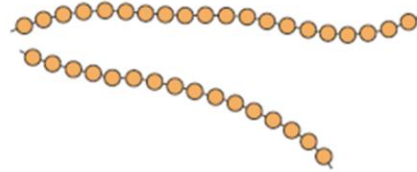
Bulky side groups, such as aromatic ring structures, also greatly restrict the mobility of the chain.



Molecular structures

Linear polymers: Those in which the repeat units are joined together end to end in single chains.

Chains are flexible.



Van der Waals forces act between the chains.

Examples - polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and the fluorocarbons.

Adapted from Fig.
14.7, Callister &
Rethwisch 8e.

The final characteristics of a polymer material depend not only on the molecular weight and shape of the chains, but also variations in the structure of the chains and how they associate with each other.

Linear polymers are those in which the repeat units are joined together end to end in single chains. The chains are long and flexible, and in most cases having extensive secondary bond interactions between the chains. Example of linear polymers are polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and some of the fluorocarbons.



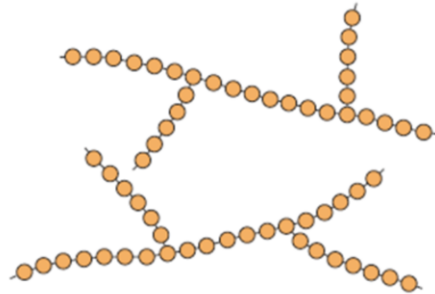
Molecular structures

Branched polymers: Contain side-branch chains which are connected to the main ones.

Branches are considered to be part of the main-chain molecule.

Reduced chain packing efficiency
- lower density.

Examples - Low density polyethylene (LDPE) contains short chain branches.



Adapted from Fig.
14.7, Callister &
Rethwisch 8e.

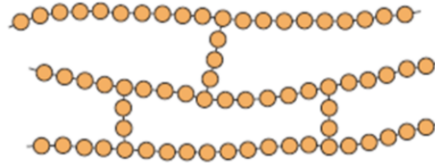
Branched polymers contain side-branch chains which are connected to the main ones, however, these branches are considered to be part of the main-chain molecule.

The presence of branches reduces the packing efficiency of the chains, and therefore lowers the density of the polymer, relative to those of linear chain species. An example of a branched polymer is LDPE, which contains short chain side branches.



Molecular structures

Cross-linked Polymers: Adjacent linear chains are joined one to another at various positions by covalent bonds.



Adapted from Fig.
14.7, Callister &
Rethwisch 8e.

Rubber is usually cross-linked elastic materials (vulcanization).

With cross linked polymers, adjacent linear chains are joined one to another at various positions by covalent bonds. Rubber – polyisoprene - is usually crossed linked as part of the vulcanisation process.



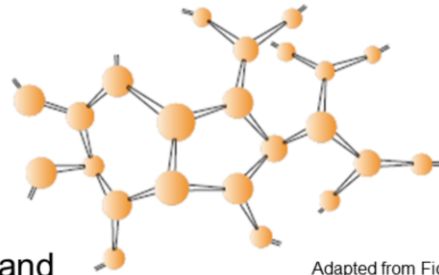
Molecular structures

Network Polymers: Multifunctional monomers forming three or more active covalent bonds.

Highly cross-linked polymers may also be classified as a network polymers.

These have distinctive mechanical and thermal properties.

Examples: epoxies, polyurethanes, and phenol-formaldehyde resins.



Adapted from Fig.
14.7, Callister &
Rethwisch 8e.

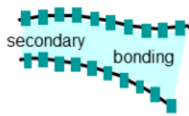
Network Polymers are formed from multifunctional monomers forming three or more active covalent bonds. Highly cross-linked polymers may also be classified as a network polymers. These materials have distinctive mechanical and thermal properties. When a networked polymer is heated, the covalent cross-linking effectively locks the chains in place and the structure remains solid. This type of polymer is called a thermoset. Earlier in this summary we looked at Bakelite as an example of a thermoset.

Polymers with a small degree of cross-linking are elastomers. In this case the cross-linking is not abundant enough to prevent the structure from changing somewhat as it is heated, but it's enough to prevent the chains slipping past each other entirely. Elastomers recover really well from deformation, as the crosslinks they do have supply a force to pull the chains back to their predeformed state.



Molecular structures

Polymer chain configurations and strength:



Linear



Direction of increasing strength

Adapted from Fig. 14.7, Callister & Rethwisch 8e.

So we've now introduced four different types of polymer molecular structure; linear, branched, cross linked and networked. The type of polymer chain structure dictates to some extent the tensile strength of the resulting polymer, and you can see that effect illustrated here.

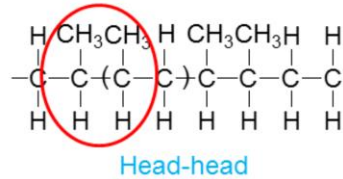
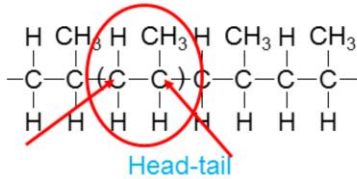
The linear polymers interact by relatively weak intermolecular bonds, whilst branched polymers interact through entanglements, twists and secondary bonding. Crosslinked, and networked polymers are bound by strong covalent bonding, and the tensile strength increases correspondingly.



Molecular Configurations

Molecular configuration describes:

- The **direction** in which monomers are linked together



- The **order** in which monomers are joined together (for copolymers)

The **configuration** is fixed during synthesis, and **cannot be changed without breaking and reforming bonds**.

Molecular configuration is a property that describes the direction in which the monomers are joined together. If we look at the polypropylene chain here, we could consider the repeat unit as having a 'head' end (the CH₂, here) and a 'tail' (the CHCH₃ group, here). The molecular configuration in this case is then head to tail, along the chain. The methyl groups are on every other carbon. Here, however, the configuration is head to head, and the methyl groups sit next to each other.

The order in which monomers are joined together is also described by the configuration. This is obviously only relevant for polymers with more than one type of monomer.

The **configuration** is fixed during synthesis, and **cannot be changed without breaking and reforming bonds**



Tacticity

Tacticity: Stereoregularity of the chains.

Earlier in this summary, we introduced the idea of isomerism, the situation where two compounds have identical chemical compositions, but different structures. We're now going to expand that idea and define two subclasses of isomerism, namely geometric isomerism, and stereoisomerism.

Stereoisomers are isomers that differ only in the spatial orientation of their component atoms; how they are arranged three dimensionally.

Stereoregularity, or tacticity, describes the regularity of the side group orientations on the backbone.

The side groups of isotactic polymers are all situated on one side of the chain.

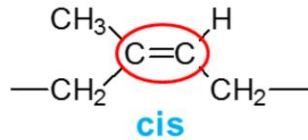
In an syndiotactic configuration, the side groups sit on alternate sides of the chain.

In atactic polymers the side-group orientations are random along the chain.



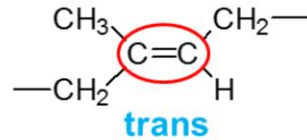
cis/trans isomerism

Possible within repeat units having a double bond between chain carbon atoms.



cis-isoprene
(natural rubber)

bulky groups on same
side of chain



trans-isoprene
(gutta percha)

bulky groups on opposite
sides of chain

Conversion of **trans** to **cis**, or vice versa, is not possible by a simple chain bond rotation because the chain double bond is extremely rigid.

Geometrical isomerism is a feature of repeat units containing a double bond. Each carbon atom participating in the double bond also has an attached side group, and these may sit on one side of the bond, or the other. In the cis-configuration, both side groups are on the same side of the polymer chain. In the trans configuration, they sit on opposite sides of the chain. Note that because it's not possible to rotate around the double bond, it isn't possible to convert from one configuration to the other.



Summary

- Most polymers are composed of **repeat units** of very long molecular **chains** of carbon covalently bound with other elements.
- Polymers are synthesized by **addition** or **stepwise polymerisation**.
- The average molecular weight of a polymer is defined as **number average molecular weight** or **weight average molecular weight**.
- The **structure of the molecular chain** has a strong influence on the final physical structure of the polymer.

To summarise what we have covered in this lecture summary, polymers are composed of repeat units forming long chains of carbon, covalently bound with other elements.

Polymers are synthesized by either addition or stepwise polymerization.

The average molecular weight of a polymer is defined by either the number average molecular weight, or the weight average molecular weight.

The structure of the molecular chains within a polymer has a strong influence on its final physical structure.



Thank you

If you have any questions or desire further clarification please post a question or comment on the Discussion Forum.