



STRUCTURE

2.4

From models to materials

◀ False-colour scanning electron micrograph (SEM) of a 'hook and loop' material, used as a reversible fastener on clothing and fabric. It is a two-sheet nylon structure with hooks on one surface (right) and loops on the other (left). When the two sheets are pressed together, the hooks attach to the loops, giving a secure grip but one that can be easily undone. Hook-and-loop fasteners are an example of an innovative material that has been designed by application of models of bonding and structure.

Guiding question

What role do bonding and structure have in the design of materials?

From early history, humans have worked to transform readily available natural resources into more useful materials. Civilizations are sometimes characterized by the technology they have developed to accomplish this. The Bronze Age, for example, marks the time when copper was first produced from smelted ores. The extraction of iron from its ores in the blast furnace is probably one of the most significant developments in the Industrial Revolution of the 18th century. These technological advances, however, were largely based on empirical discovery and usually came without a full understanding of the underlying scientific principles.

As the models we use to explain chemical structure and bonding have advanced, so has our ability to predict the properties of materials. This has enabled us to design structures for specific purposes. Materials that have transformed everyday life, such as superconductors, breathable fabrics and liquid crystals, are only in existence because we have been able to apply advanced bonding theory to their synthesis.

In this chapter, we first develop a more holistic model of bonding from the three discrete models of ionic, covalent and metallic bonding discussed earlier. This gives us a tool, the bonding triangle, which helps to predict the properties of unknown and new substances. We describe alloys, which are mixtures of metals, as an example of how changing the bonding within a structure can enhance the resulting properties and uses of a material. Finally, we consider the structure of polymers, which include all plastics. These materials have made such a significant impact, both in terms of convenience in our lives and with respect to some of their damaging environmental effects, that it is suggested the current age may become known as the Plastic Age.

As the models we use to explain structure and bonding will continue to evolve, so will our ability to develop materials fit for purpose. This innovation in material science must be accompanied by application of Green Chemistry principles to control the wider impact of these developments on health and the environment.

Structure 2.4.1 – The bonding triangle

Structure 2.4.1 – Bonding is best described as a continuum between the ionic, covalent and metallic models, and can be represented by a bonding triangle.

Use bonding models to explain the properties of a material.

A triangular bonding diagram is provided in the data booklet.

Structure 3.1 – How do the trends in properties of period 3 oxides reflect the trend in their bonding?

Nature of Science, Structure 2.1, 2.2 – What are the limitations of discrete bonding categories?

Properties of ionic and covalent compounds. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS



To what extent do the classification systems we use in the pursuit of knowledge affect the conclusions that we reach?

TOK

The bonding triangle is fully described as the 'van Arkel-Ketelaar triangle of bonding' after the two Dutch chemists credited with its development in the mid-20th century. Anton van Arkel first proposed the triangle and applied it mostly to elements. Jan Ketelaar extended his ideas to more compounds. Others worked in this field and used various parameters to describe the properties of the bonded atoms, but electronegativity values became the established basis for determining positions in the triangle.

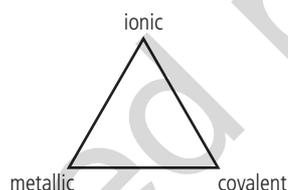
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The bonding triangle. Calculations of the electronegativity difference and the average electronegativity of the bonded atoms determine the position of a material in the triangle. In turn, this position helps to predict the properties of a material.

Chemical bonding is best described as a continuum rather than as discrete bonding types

In Structure 2.1, 2.2 and 2.3 we discussed the three models of bonding – ionic, covalent and metallic – as separate categories. Although there are materials that can be described by one of these models alone, often such a classification is an oversimplification as most materials are an intermediate between these three bonding types, and so show intermediate properties. We have already encountered this concept in Structure 2.2 with the description of polar bonds, which show some ionic character present in covalent bonds.

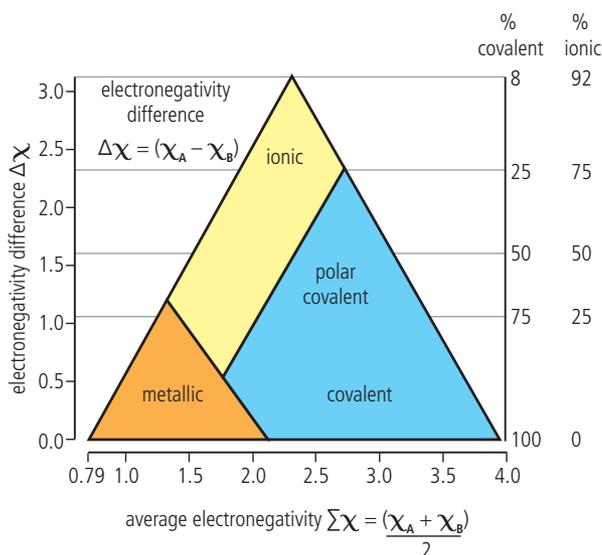
Therefore, a more accurate picture of bonding is a **continuum** where the different bonding types are present to different degrees. The simplest representation of this is a triangle where each vertex represents one of the three models of bonding. Different materials are then scattered through the triangle, positioned according to the relative amount of each type of bonding they contain.



▲ A simple bonding triangle showing the three main types of bonding.

The position of an element or compound in the bonding triangle is determined from its electronegativity values, as these give a measure of the tendency of an atom to gain electrons, and therefore the type of bond it will form. Electronegativity values are given in Section 8 of the data booklet, and are shown with the symbol χ . The bonding triangle uses the following axes:

- x-axis: average electronegativity of bonded elements A and B: $\Sigma\chi = \frac{\chi_A + \chi_B}{2}$
- y-axis: electronegativity difference of bonded elements A and B: $\Delta\chi = \chi_A - \chi_B$



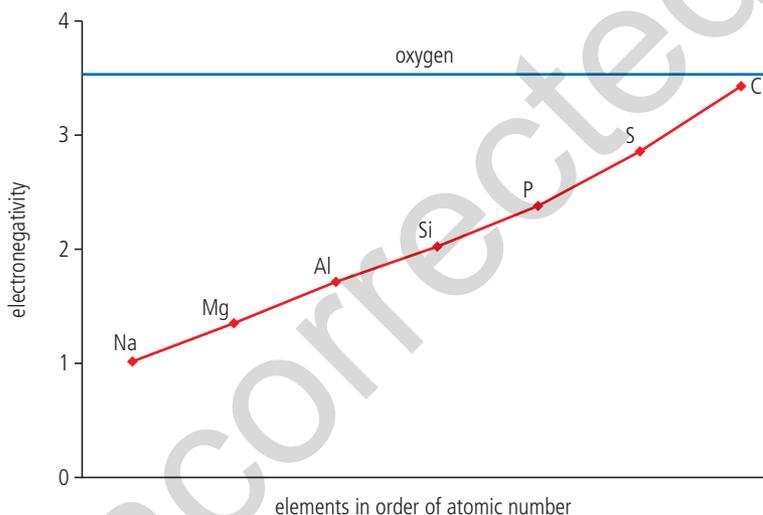
Elements have zero electronegativity difference between their atoms, and so are positioned on the *x*-axis, metals on the left (low electronegativity) and non-metals on the right (high electronegativity). Ionic compounds with high electronegativity difference are found at the top centre, while covalent compounds with low electronegativity difference are found in the lower right corner. Polar covalent compounds occupy the intermediate position.

From these positions in the triangle and knowledge of the characteristics of each bonding type, we are able to deduce the expected properties of a material.

Nature of Science

The bonding triangle is a tool that has predictive power for the properties of a substance.

We can illustrate the importance of electronegativity values in determining the type of bonding by looking at the oxides of the elements in period 3. Oxygen has an electronegativity value of 3.4, and as we move from left to right across period 3, the electronegativity of the elements increases and approaches this value, as shown in Figure 1.



S2.4 Figure 1 Electronegativity values of the elements of period 3 increase across the period, approaching the value of oxygen.

As the *difference* in electronegativity values decreases, so too does the ionic character of the oxides, while the covalent character increases. This trend in bonding explains the trend in physical properties of the period 3 oxides as summarized below.

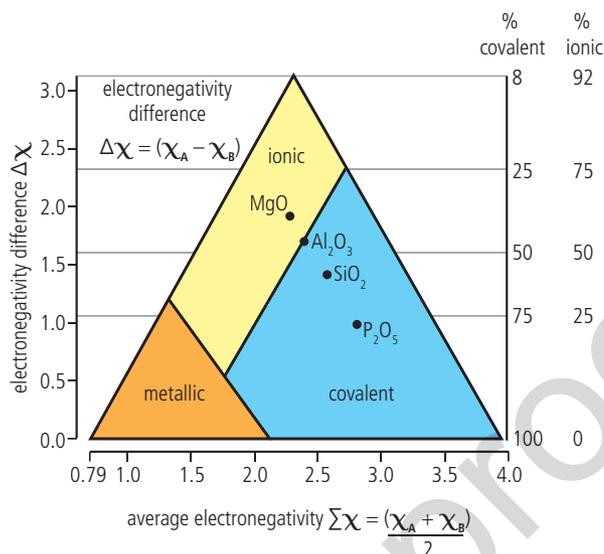
	Na_2O , MgO and Al_2O_3	SiO_2	P_4O_{10} , SO_2 and Cl_2O
properties	high melting and boiling points, electrical conductors when molten	high melting and boiling points, non-conductor of electricity	low melting and boiling points, non-conductors of electricity.
bonding	ionic metallic oxides	giant covalent oxide of the metalloid silicon	covalent non-metallic oxides

This periodic trend could be predicted by considering the positions of the oxides in the bonding triangle, as shown in Figure 2.

SKILLS

Cement and mortar: investigating the parameters that affect their properties. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Structure 3.1 – How do the trends in properties of period 3 oxides reflect the trend in their bonding?



S2.4 Figure 2 The bonding triangle showing the positions of the oxides of period 3 elements. These positions reflect the trend in their bonding, and enable us to predict and explain the trend in their properties.

We have described the classification of bonds into ionic, covalent or metallic as an over-simplification as it can lead to incorrect predictions of physical properties. For example, aluminium chloride, AlCl_3 , containing a metal and a non-metal might be classified as ionic, which would suggest a high melting point. Yet the melting point of AlCl_3 is significantly lower than that of a similar sized ionic compound such as NaCl .

- NaCl mp 801°C
- AlCl_3 mp 192°C

When we determine the positions of these compounds in the bonding triangle (see page 264), we find that AlCl_3 has significant covalent character, and this explains its relatively low melting point. The model of a bonding continuum in the bonding triangle allows us to make more accurate predictions of properties.

Structure 2.4.2 – Application of the bonding triangle

Structure 2.4.2 – The position of a compound in the bonding triangle is determined by the relative contributions of the three bonding types to the overall bond.

Determine the position of a compound in the bonding triangle from electronegativity data.

Predict the properties of a compound based on its position in the bonding triangle.

To illustrate the relationship between bonding type and properties, include example materials of varying percentage bonding character. Only binary compounds need to be considered.

Calculations of percentage ionic character are not required.

Electronegativity data are given in the data booklet.

Structure 2.1, 2.2, 2.3 – Why do composites such as reinforced concretes, which are made from ionic and covalently bonded components and steel bars, have unique properties?

Nature of Science, Structure 2.1, 2.2 – What are the limitations of discrete bonding categories?

Electronegativity values → position of a material in the bonding triangle → prediction and explanation of many properties.

Composite materials have been made by humans for thousands of years. One of the earliest examples is adobe bricks, which are made from a combination of mud and an organic material such as straw or dung. Dried mud alone is brittle, straw is very strong but difficult to hold in place. The combination produces a material which is strong and easy to shape.



In the previous section, we considered the bonding in AlCl_3 and NaCl . We can determine the positions of these compounds in the bonding triangle, and estimate their percentages of bonding type from the right-hand scale of the triangle.

Substance	χ_{average}	$\Delta\chi$	Position in triangle	Bonding
NaCl	$\frac{0.9 + 3.2}{2} = 2.05$	$3.2 - 0.9 = 2.3$	upper centre	ionic compound, approximately 75% ionic
AlCl_3	$\frac{1.6 + 3.2}{2} = 2.4$	$3.2 - 1.6 = 1.6$	centre, close to the ionic and covalent border	polar covalent, approximately 50% covalent

Composite materials, such as fibreglass and concrete, are heterogeneous mixtures of at least two different materials, which are present as separate phases. As these are mixtures, each component retains its individual properties. The result is a material with enhanced properties designed for specific purposes.

Structure 2.1, 2.2, 2.3 – Why do composites such as reinforced concretes, which are made from ionic and covalently bonded components and steel bars, have unique properties?



Adobe bricks drying in the sun in Peru. ▶



Construction of a stadium. Reinforcing metal bars (rebar) are fitted before pouring concrete. Concrete is strong in compression but weak in tension. The rebar significantly improves the tensile strength and ductility of concrete structures. ▶



Exercise

- Q1.** Use data from Section 9 and Section 17 of the data booklet to classify the bonding in the following materials:
 (a) Cl_2O (b) PbCl_2 (c) Al_2O_3 (d) HBr (e) NaBr
- Q2.** Copper(II) oxide can be added to give glass a green or blue colour. Deduce the position of copper oxide in the bonding triangle and describe the nature of its structure and bonding.
- Q3.** Silicon dioxide and aluminium oxide are important minerals in the Earth's crust. Use the bonding triangle to deduce their positions and so determine which has the greater covalent character.

Structure 2.4.3 – Alloys

Structure 2.4.3 – Alloys are mixtures of a metal and other metals or non-metals. They have enhanced properties.

Explain the properties of alloys in terms of non-directional bonding.

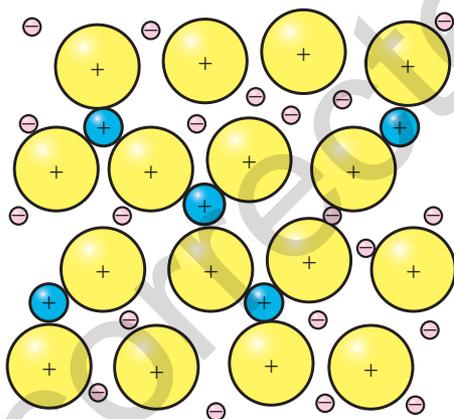
Illustrate with common examples such as bronze, brass and stainless steel.

Specific examples of alloys do not have to be learned.

Structure 1.1 – Why are alloys more correctly described as mixtures rather than as compounds?

Alloys are solutions of metals with enhanced properties

Alloys are produced by adding one metal element to another metal (or carbon) in the liquid state, so that the different atoms can mix. As the mixture solidifies, ions of the different metals are scattered through the lattice forming a structure of uniform composition. Alloys contain metallic bonds as the delocalized electrons bind the lattice. The production of alloys is possible because of the non-directional nature of the delocalized electrons, and the fact that the lattice can accommodate ions of different size.



▲ Alloys consist of different metal ions and a sea of delocalized electrons. The smaller cations (blue) are able to fit in the spaces between the larger cations (yellow) in the lattice structure.



◀ Molten metal being poured from a vat at the Magnitogorsk iron and steel works, one of the largest metal working plants in Russia. The production of alloys depends on mixing metals in the molten state.

SKILLS

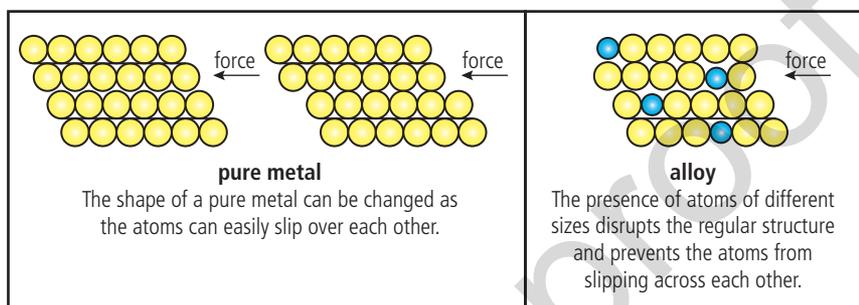
Making polymers. Full details of how to carry out this experiment with a worksheet are available in the eBook.



Alloys are homogeneous mixtures containing at least one metal, and held together by metallic bonding.

Alloys have some properties that are distinct from their component elements due to the different packing of the cations in the lattice. The regular arrangement of atoms in a pure metal is interrupted in the alloy by the presence of different cations, making it more difficult for atoms to slip over each other and so change the shape. The alloy is often stronger, more chemically stable, and more resistant to corrosion than its component elements. For example, steel, which is an alloy of iron with less than 2% carbon and 1% manganese and other trace elements, can be 1000 times stronger than iron.

Changing the regular packing in the lattice gives alloys enhanced properties compared with the pure metal.



Some examples of common alloys are given below.

Name of alloy	Component metals	Properties and uses
steel	iron with carbon and other elements	high tensile strength but corrodes, used as structural material
stainless steel	iron with other elements such as nickel and chromium	widely used in domestic and industrial appliances due to strength and corrosion resistance
brass	copper and zinc	variety of plumbing fittings
bronze	copper and tin	coins, medals, tools, heavy gears
pewter	tin and antimony and copper	decorative objects
duralumin	aluminium, copper and manganese	aircraft, boats and machinery due to high strength and resistance to corrosion
nichrome	nickel and copper	heating elements in toasters, electric heaters
solder	lead and tin	joining two metals together, especially in electric circuitry
sterling silver	silver and copper	jewellery, art objects

Alloys, in common with other mixtures, have no fixed composition. For example, 'steel' is the general name for a mixture of iron and carbon and other metals in different proportions. So, unlike compounds, alloys cannot be represented by a chemical formula. Alloys form by mixing liquid metals without chemical reaction, and so the components retain metallic properties such as thermal and electrical conductivity, and magnetism in the case of iron-containing alloys.



Nichrome wire, an alloy of nickel and copper, is used when carrying out flame tests in the laboratory. It is a convenient material because it is resistant to oxidation at high temperatures. The lilac colour here indicates that the sample contains potassium.



Structure 1.1 – Why are alloys more correctly described as mixtures rather than as compounds?

Steel manufacture is one of the world's largest industries and is sometimes used as a measure of a country's development and economic progress. Global steel production has tripled in the last 50 years, with China and India becoming the world's top steel-producing nations. Steel is the foundation of buildings, vehicles and industries, including sustainable energy technologies. Plans for sustainability of steel production include moving towards a fossil-fuel-free industry by removing coal from the process. Steel is infinitely recyclable with no loss of quality, and it is estimated that new steel products contain on average 30% recycled steel.

▲ Swedish steel-making company SSAB has plans to eliminate its use of coal in its plants by 2045. The company uses hydrogen, produced using clean-energy powered electrolysis, in place of coal – dramatically reducing carbon pollution. The first fossil-fuel-free steel was produced in 2020, and will be brought to market in 2026.

Challenge yourself

- The components of a mixture can usually be separated by physical means. What might be the challenges of trying to separate the metals from an alloy?

Exercise

- Q4.** An alloy is a mixture of metal with which of the following?
- A a second metal or other non-metal material
 - B a non-metal material only
 - C a second metal only
 - D none of the above
- Q5.** Which of the following is not an alloy?
- A solder B silver C bronze D brass
- Q6.** Explain how alloying can modify the structure and properties of metals.
- Q7.** What is the difference between an alloy and a composite?

Structure 2.4.4 – Polymers

Structure 2.4.4 – Polymers are large molecules, or macromolecules, made from repeating subunits called monomers.

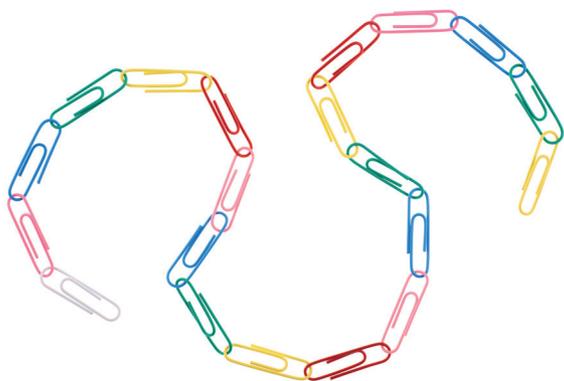
Describe the common properties of plastics in terms of their structure.

Examples of natural and synthetic polymers should be discussed.

Structure 2.3 – What are the structural features of some plastics that make them biodegradable?

The polymers described in this chapter are organic compounds, based on the covalent chemistry of carbon and its unique ability to form stable bonds with itself, with hydrogen and with other elements. To understand these structures, you may find it helpful to first study an introduction to organic chemistry in Structure 3.2.

Polymers are large molecules made from repeating subunits

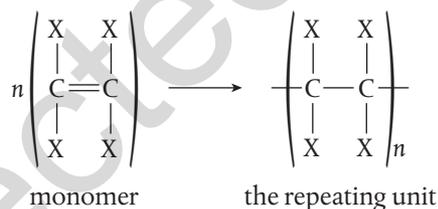


▲ We can think of polymer formation as similar to making a chain of paper clips.

Some small molecules, known as **monomers**, are able to react together to form a linked chain held together by covalent bonds, known as a **polymer**.

Polymers are also known as **macromolecules**, as they are composed of thousands of atoms and so are relatively large compared with other molecules. Polymers vary in the nature of the monomer, and the length and the amount of branching in the chain, and so have a wide range of different properties.

As polymers are such large molecules, we show their structure as a **repeating unit**, which has open bonds at each end. It is put in a bracket with n , the number of monomers in the polymer, as subscript.



This is an example of an addition polymer, described below.

Nature of Science

Although plastics were one of the key materials of the 20th century, the notion of very large molecules was not widely accepted by the scientific community until 1929. Hermann Staudinger, a German organic chemist, pushed forward his idea of macromolecules, which he characterized as polymers. He experienced widespread resistance from his academic peers who thought that the newly invented plastics and natural materials such as rubber, starch, and cellulose were bundles of small molecules held together by unknown intermolecular forces. Staudinger's idea that there was a covalent bond between the units had little support. He was told by one of his colleagues to 'drop the idea of large molecules.' The eventual acceptance of Staudinger's theory was a key step in our understanding that led to the practical development of polymer chemistry. Science is a human activity and it sometimes takes courage to challenge the accepted models of the time.

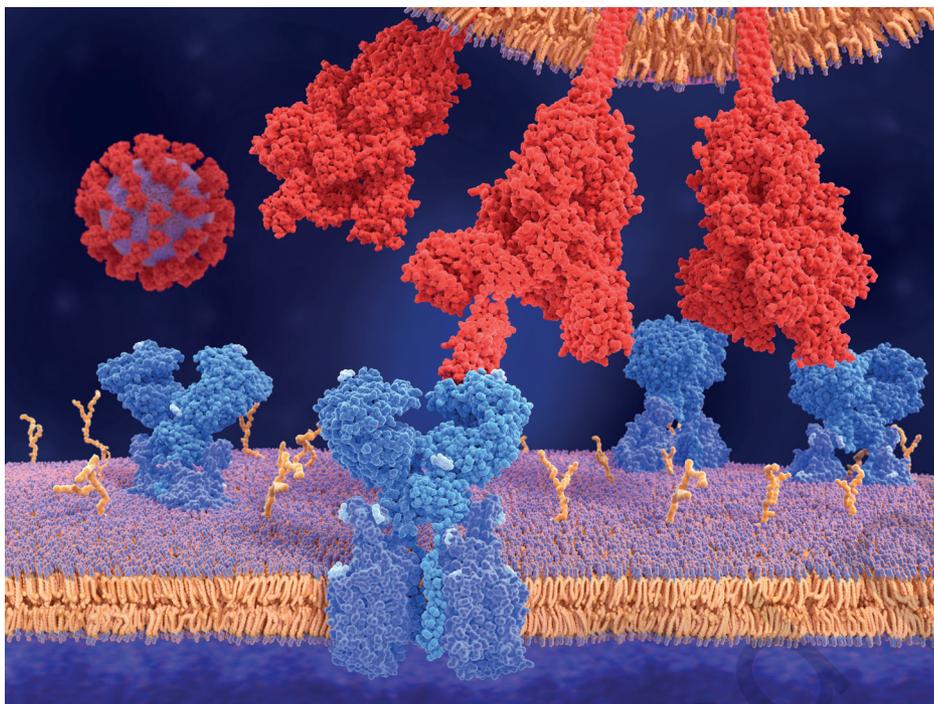
Polymers are widespread in living things. Molecules such as protein, starch and DNA are examples of **natural polymers**. Understanding the relationship between the structure and function of these molecules has been a major focus of biochemical research over the last 100 years. Many advances in medicine, such as vaccines and drugs, have been developed from knowledge of the detailed structure and interaction of these polymers.

Hermann Staudinger was the first polymer chemist to be awarded the Nobel Prize in Chemistry in 1953 'for his discoveries in the field of macromolecular chemistry'.

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Does competition between scientists help or hinder the production of knowledge?

TOK



◀ Molecular model of a coronavirus spike protein (shown in red) bound to human cell receptors (shown in blue). Binding between the spike protein and the receptor enables the virus to enter the human cell, where it replicates itself and can cause disease. Analysis of the structure of the viral protein, a natural polymer, is critical in enabling researchers to develop vaccines against diseases such as Covid-19.

Human-made polymers, known as **synthetic polymers**, first appeared in the 1930s when raw materials from the petroleum industry became available. This rapidly led to the development of a wide range of new materials known as **plastics**, a trend which continues to this day. Plastics are synthetic polymers that have widespread uses due to their light weight, low reactivity, water resistance and in some cases their strength. We use plastics in almost every aspect of daily life including packaging, construction, clothing, transportation and machinery. As a result, plastics have become widely distributed in both terrestrial and marine environments.

The very features that make plastics so useful, such as their unreactivity and water repellency, mean they are often **non-biodegradable**, that is, they cannot be broken down by natural processes, and so remain in the environment for indefinite periods of time. Accumulation of plastics in natural environments is one of the largest and most pressing environmental concerns of our time.



▲ Plastic waste washed up on beach in Ireland. Common plastics include polythene, PVC, nylon, polystyrene and Kevlar®.



Global production of plastics has increased exponentially since 1950 and continues to rise. It is suggested that fossilized plastics may form a distinctive stratal layer, possibly marking the start of the proposed geological epoch the 'Anthropocene', the time of significant human impact on Earth's geology and ecosystems. A high proportion of plastics end up in the oceans where they have a widespread impact on the ecosystem. It is estimated that by 2030 there could be 300 million tonnes of accumulated plastic in the oceans. While measures to try to address this include more efficient recycling processes, biodegradable plastics, and plastic-feeding microorganisms, the urgent need is to reduce the source. We can all share some responsibility for decreasing our use of disposable plastics.

Properties of polymers.
Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS



Structure 2.3 – What are the structural features of some plastics that make them biodegradable?



Close-up of clear plastic pellets made from corn (Zea mays, top) starch. Sugar from corn is fermented to produce lactic acid which undergoes further reaction to yield long-chain molecules called polylactide (PLA). The plastic is biodegradable and can be used for both food and non-food packaging as well as textiles and other materials.



There is growing evidence that some microorganisms are evolving to break down plastic in their habitat.



Genetic analysis of bacteria from different environments has found enzymes that can degrade different types of plastic, where the number and type of enzymes matches the amount and type of plastic pollution in different locations. For example, in ocean studies, higher levels of degrading enzymes were found at levels of 200–600 m below the surface, matching the higher levels of plastic pollution known to exist at these depths.

There is potential to develop these microbial communities for targeted degradation of specific polymers.



Nature of Science

It is hard to assess the scale of the impact that plastics have had on society. The manufacture of diverse plastics has brought innovation and progress to our global food supply, clothing, health care and infrastructure. Yet these innovations have come at significant cost to the environment, and the long-term consequences are still being determined. While scientific progress is responsible for both the intended and unintended consequences, it is scientists who must respond to the problems.

Structure 2.4.5 – Addition polymers

Structure 2.4.5 – Addition polymers form by the breaking of a double bond in each monomer.

Represent the repeating unit of an addition polymer from given monomer structures.

Examples should include polymerization reactions of alkenes.

Structures of monomers do not have to be learned but will be provided or will need to be deduced from the polymer.

Structure 3.2 – What functional groups in molecules can enable them to act as monomers in addition reactions?

Reactivity 3.1 – Why is the atom economy 100% for an addition polymerization reaction?

Atom economy is a measure of the proportion of reactant that ends up in the desired product, based on the reaction's stoichiometry.

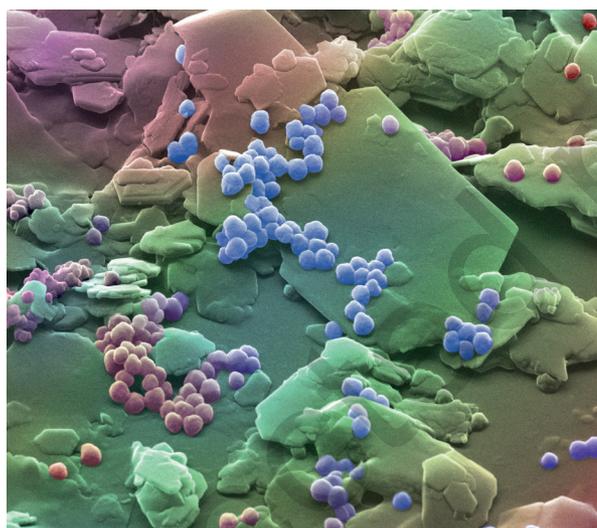
$$\% \text{ atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

Addition polymerization reactions do not generate a by-product and so convert 100% of reactants into product. This does not mean, however, that there is no waste or environmental impact of these reactions. A reaction yield of less than 100% means there will be unreacted monomer at the end of the process. Also, many polymerization reactions use solvents and conditions of high temperature, pressure and/or catalysts – all of which must be considered as part of an environmental assessment of the process.

Reactivity 3.1 – Why is the atom economy 100% for an addition polymerization reaction?

Microplastics are small plastic pieces less than 5 mm long, which harm marine life and enter the food chain. Microplastics come from a variety of sources, including from larger plastic debris that degrades into smaller and smaller pieces.

Microbeads are a type of microplastic, mostly derived from health and beauty products that pass through water filtration systems.



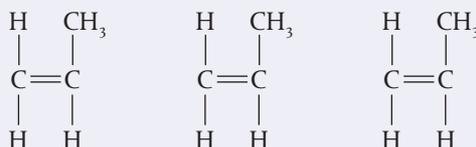
Coloured scanning electron micrograph (SEM) of particles found within a cosmetic facial scrub. A single shower can result in 100 000 plastic particles entering the ocean. Legislation to ban the use of microbeads is currently under discussion in many countries.

Worked example

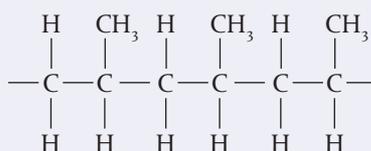
Deduce the structure of the addition polymer formed from methylpropene. You should include three repeating units in the structure.

Solution

1. Draw three structures with the alkene double bond in the middle:



2. Open the double bond in each molecule so that single bonds extend in both directions:



Challenge yourself

2. Draw the repeating unit in polystyrene, given that the formula of the monomer is $C_6H_5CHCH_2$.



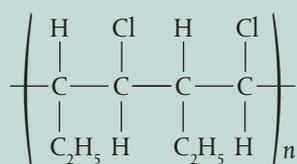
Addition polymers are found almost universally in daily life. Poly(ethene) has excellent insulating properties and is commonly used in household containers, water tanks, and piping. Polypropylene is used in the manufacture of clothing, especially thermal wear for outdoor activities. PVC is used in all forms of construction materials, packaging, electrical cable sheathing, etc. There is controversy regarding its use, linked to health and environmental concerns, because of its high chlorine content which makes it difficult to recycle. Some countries are banning the use of PVC in packaging. PTFE has a very low surface friction so is widely used in non-stick pans. It also makes up one of the layers in waterproof, breathable fabrics such as GoreTex®. The resistance of PTFE to van der Waals' forces means that it is the only known surface to which a gecko cannot stick.

Exercise

- Q8. What do poly(ethene) and ethene have in common?

- A same molecular formula
- B same empirical formula
- C physical properties
- D chemical properties

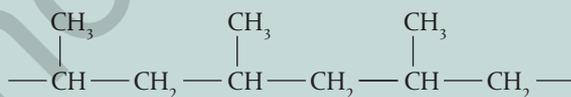
- Q9. The repeating unit of a polymer is shown:



Which structure shows the monomer used to make this polymer?

- A $\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{Cl} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$
- B $\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{Cl} \quad \text{H} \end{array}$
- C $\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{H} \\ | \quad | \\ \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{Cl} \end{array}$
- D $\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{H} \\ | \quad | \\ \text{C}=\text{C} \\ | \quad | \\ \text{Cl} \quad \text{H} \end{array}$

- Q10. Part of the structure of a polymer is shown:



Which is the formula of the monomer used to make this polymer?

- A C_3H_6 B C_6H_{12} C C_3H_8 D C_6H_{14}

- Q11. Distinguish between the terms recyclable, biodegradable and reusable as applied to plastics. What are the advantages and disadvantages of each of these in helping to reduce the environmental impact of plastics? What other ways can we help to reduce the amount of plastic waste accumulating in the oceans?

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Structure 2.4.6 – Condensation polymers

Structure 2.4.6 – Condensation polymers form by the reaction between functional groups in each monomer with the release of a small molecule.

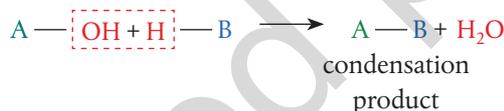
Represent the repeating unit of polyamides and polyesters from given monomer structures.

All biological macromolecules form by condensation reactions and break down by hydrolysis.

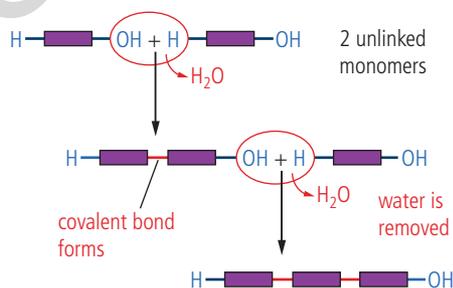
Structure 3.2 – What functional groups in molecules can enable them to act as monomers in condensation reactions?

Monomers with two functional groups can be used to make condensation polymers

Condensation reactions occur when two functional groups react to form a new covalent bond, with the release of a small molecule, such as H_2O .



In order to form condensation polymers, monomers must each have *two functional groups*, which we can think of as ‘active ends’ where condensation reactions can occur. This allows them to form new covalent bonds with neighbours on both sides. It is similar to the way in which people can only form a human chain when they have two available hands to link with neighbours. A small molecule such as H_2O , HCl or NH_3 is released as each new bond forms.



▲ Condensation reactions involve the loss of a small molecule for every covalent bond formed.

To take part in condensation reactions, the functional groups in neighbouring molecules must be able to react together. Two common examples are considered here.

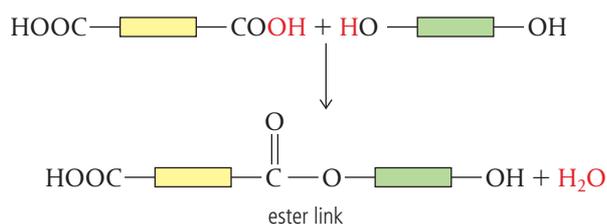
1. Carboxylic acid and alcohol react to form polyester

When one monomer has two carboxylic acid, $-\text{COOH}$, groups, and the other monomer has two alcohol, $-\text{OH}$, groups, an **ester link** forms between them. The chain extends in both directions and is therefore known as a **polyester**.

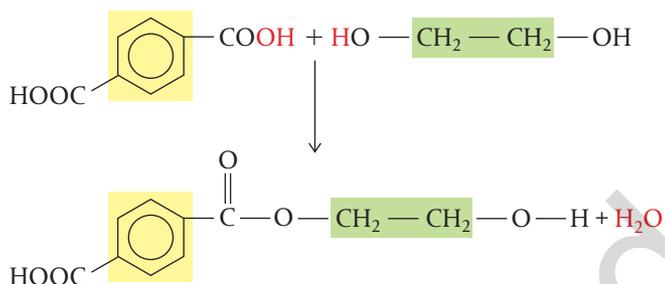
When describing these reactions it is sometimes helpful to think about the functional groups sticking out in both directions as if from a box, which represents the rest of the molecule.

Condensation polymers form between monomers which each have two functional groups to react. A small molecule is released for each covalent bond that forms between the monomers.

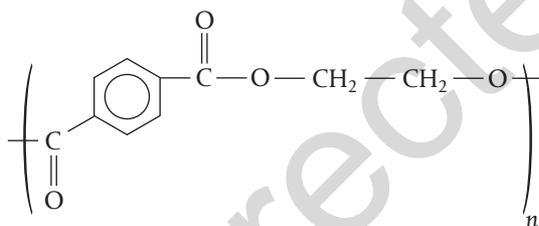
For example:



When we focus on the functional groups in this way, it is easier to deduce the repeating unit from any specified monomers. For example, formation of a polyester from the monomers benzene-1,4-dicarboxylic acid and ethane-1,2-diol is shown below.



The repeating unit of this polymer is:



This polyester, polyethylene terephthalate, is often abbreviated to PET and is widely used in synthetic fibres, plastic bottles and other containers. Other polyesters include the natural polymers in fats and oils, and phosphodiester links in the nucleic acids, DNA and RNA.

When we recognize the linkage between two monomers, we can work backwards to deduce the monomers that combined by condensation.



You can learn more about naming and representing organic molecules in Structure 3.2, Functional groups.

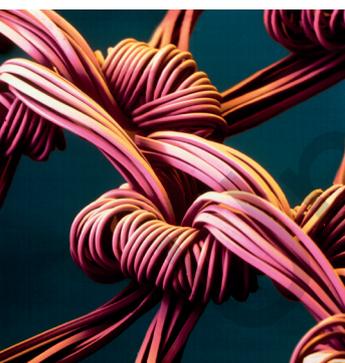


Make sure when you draw a repeating unit of a polymer that you show open bonds extending through the brackets on each end of the molecule, as this shows the ability of the molecule to link with additional monomers.



Bottles being processed at a PET recycling plant. PET is the most common plastic used in drink bottles and food containers and can be fully recycled through washing and remelting. Recycled PET is used to make new containers, carpets and fleece clothing.

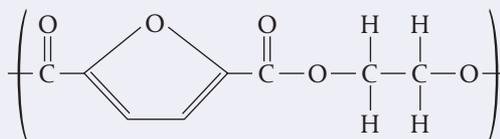
Commercial production of nylon began in 1939, just before the start of the Second World War. Its discovery in 1935 was the result of research by American chemists, notably Wallace Carothers working for the DuPont company. He was looking for a synthetic fibre to replace silk because the supply of silk from Japan was vulnerable to the worsening trade relations with America. When nylon was first produced, it was heralded as being 'as strong as steel, as fine as a spider's web.' One of the earliest major products was women's stockings – 64 million pairs were sold during the first year. Nylon was used in the Second World War in parachutes and tents as well as in surgical sutures. Nearly 100 years later, nylon in its various forms is still one of the most common polymers in use worldwide.



▲ Coloured scanning electron micrograph (SEM) of the weave of a nylon stocking or tights. Nylon is a polyamide with fibres that are stronger and more elastic than silk, and relatively insensitive to moisture. Nylon is used in the manufacture of textiles, moulded objects and medical sutures.

Worked example

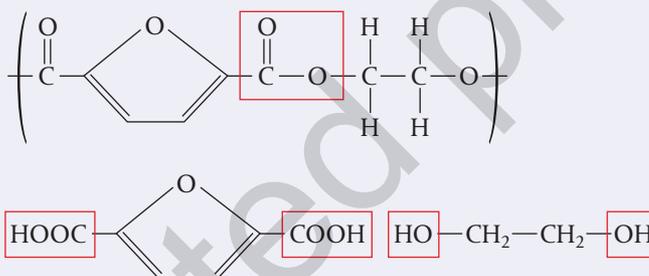
Poly(ethylene furanoate) (PEF) is a polyester made from bio-based monomers.



Deduce the structure of the two monomers from which it is made.

Solution

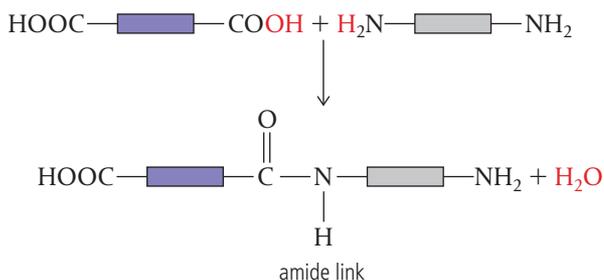
Find the ester link and break it to form an acid and an alcohol. Note that a molecule of water is added as the bond breaks.



2. Carboxylic acid and amine react to form polyamide

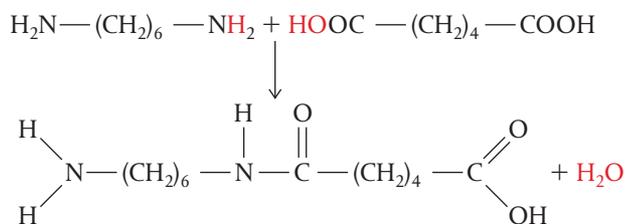
When one monomer has two carboxylic acid, $-\text{COOH}$, groups and another monomer has two amine, $-\text{NH}_2$, groups, an **amide link** forms between them. As the monomers can link with neighbours on both sides, this forms a polymer known as a **polyamide**. Polyamides can also form when monomers each have one acid and one amino group, known as amino acids.

Again, focusing on the functional groups, we can represent these reactions as follows.

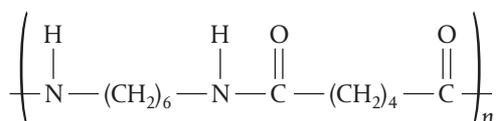


Polyamides include many synthetic polymers such as nylon and Kevlar®. They are widely used in the textile industry for clothing and carpets, as well as machine parts, tyre cords and ropes. Proteins, one of the most important and diverse types of molecules in biology, are polyamides formed by condensation reactions between amino acids.

There are several forms of nylon; the most common is called 6,6-nylon because both its monomers have six carbon atoms. The monomers are 1,6-diaminohexane and hexanedioic acid.



Therefore the repeating unit of 6,6-nylon is:



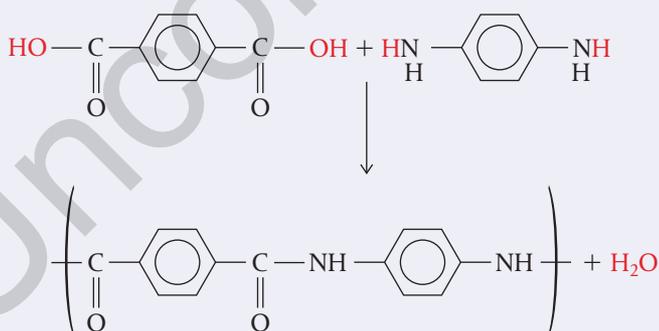
Structure 3.2 – What functional groups in molecules can enable them to act as monomers in condensation reactions?

Worked example

Use structural formulas to illustrate the reaction that occurs between benzene-1,4-dicarboxylic acid and 1,4-diaminobenzene to form the condensation polymer Kevlar®. Include the repeating unit of Kevlar® in your answer.

Solution

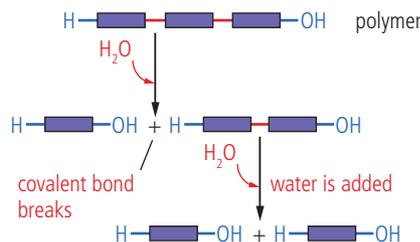
1. First draw the structures of the two monomers, positioned so that the functional groups stick out from the centre of the molecules and lie close to the functional groups on the neighbouring molecule.
2. Then deduce how the reaction between these two groups leads to loss of H₂O and the formation of a new covalent bond.



1. Use brackets to surround the structure and ensure that you have shown open bonds in the unreacted positions.
2. Include one molecule of H₂O as the product for each bond formed.

All biological macromolecules are condensation polymers, synthesized in cells by condensation reactions between monomers. For example, starch is produced by linking glucose molecules into long chains. The reverse reaction, known as **hydrolysis**, breaks the polymers down into their monomers. A molecule of water is used for each bond broken.

Hydrolysis reactions involve addition of a molecule of water for every covalent bond broken.



These hydrolysis reactions happen during digestion, decomposition and when stored materials need to be mobilized. Both condensation and hydrolysis reactions are controlled by biological catalysts called **enzymes**.

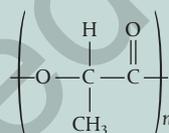


When a bulb germinates, it breaks down its food store of insoluble polymers into monomers by hydrolysis reactions. For example, the polymer starch is hydrolyzed to glucose which makes energy available for growth.

Exercise

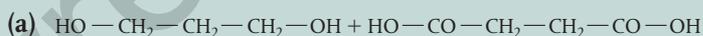
Q12. Nylon-6,10 is made from the monomers 1,6-diaminohexane and decanedioic acid. Draw the repeating unit of this polymer.

Q13. Polylactic acid is a plastic made from fermented plant starch. It has the structure below.

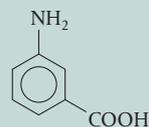


Deduce the structure of the monomer.

Q14. Draw the structures of the polymers and any by-products formed from the following pairs of monomers.



Q15. This compound is a monomer for a condensation polymer.



(a) Identify the functional groups in the monomer which allow it to act as a monomer.

(b) Deduce the by-product of the polymerization reaction.

(c) Deduce the structure of the resulting polymer. You should include at least three monomer units in your answer.

(d) Kevlar® is a polymer produced from monomers which have functional groups in the 1,4 positions of the benzene ring. Explain the strength of the polymer in terms of the orientation of the two functional groups.

(e) Explain why Kevlar® has a lower density than steel.



Guiding question revisited

What role do bonding and structure have in the design of materials?

In this chapter we used models of bonding to describe and explain the properties of some important materials.

- Bonding in materials is best described as a continuum rather than as discrete types, and can be represented as a triangle of bonding.
- The position of an element or compound in the bonding triangle is determined from electronegativity values.
- From the position of a substance in the bonding triangle, we can deduce its bonding and predict its properties.
- Alloys are homogeneous mixtures of metals with enhanced properties.
- Metals are able to form alloys because of the non-directional nature of metallic bonding.
- Polymers are macromolecules composed of subunits called monomers held together by covalent bonds.
- Addition polymers form from monomers that possess a double bond which can break to create new bonding positions for the attachment of neighbouring monomers.
- Addition polymerization reactions do not yield a by-product.
- Plastics are polymers with properties that give them widespread uses in almost all aspects of society.
- The distinct properties of plastics also cause them to accumulate in the environment without being broken down.
- Use of biodegradable plastics and recycling programs are important steps to improve the processing of plastic waste, but the urgent need is to reduce the global production of plastic.

HL

- Condensation polymers form from monomers with two functional groups which can react with the functional groups on neighbouring monomers.
- Condensation polymerization reactions release a small molecule for each covalent bond formed.
- Condensation polymers break down by hydrolysis reactions in which a small molecule is added for each bond broken in the polymer.

HL end

Practice questions

- What are alloys with two components called?

A binary alloy	B binary compound
C ternary alloy	D metallic compound
- Which of the following **cannot** be deduced from the position of an unknown substance X in the bonding triangle?
 - The chemical formula of X
 - The type of bonding in X
 - The physical properties of X
 - Whether X is an element or a compound
- Which of the following is not an addition polymer?

A polyester	B polystyrene
C poly(ethene)	D poly(tetrafluoroethene)
- In the bonding triangle, substance X is found in the top right, substance Y is found in the bottom left and substance Z is found in the bottom right. Answer the following, giving reasons for your answers:
 - Which of these substances is likely to be an element? (2)
 - For substances X and Y, give a physical property you would expect them to have in common. (2)
 - Which substance will be the most brittle? (2)
 - Which substance is likely to have the lowest boiling point? (2)

(Total 8 marks)

- Use electronegativity values from Section 9 in the data booklet to complete this table for the five substances given.

Substance	χ_{average}	$\Delta\chi$	Position in triangle and type of bonding	Predicted properties	
Sn					(2)
P ₄ O ₇					(2)
Cd ₃ Mg					(2)
MgO					(2)
NCl ₃					(2)

(Total 10 marks)

- Justify why, in terms of atom economy, the polymerization reactions of polypropylene could be considered 'Green Chemistry'. (2)
- (Total 2 marks)
- Alloys of aluminium with nickel are used to make engine parts. With reference to the model of metallic bonding, explain why this alloy is used rather than pure aluminium. (3)

(Total 3 marks)

8. Lanthanum, La, and antimony, Sb, form compounds with bromine that have similar formulas, LaBr_3 and SbBr_3 .
- (a) Determine the type of bond present in SbBr_3 , showing your method. Use Sections 9 and 17 of the data booklet. (2)
- (b) Lanthanum has a similar electronegativity to group 2 metals. Explain, in terms of bonding and structure, why crystalline lanthanum bromide is brittle. (2)
- (Total 4 marks)
9. Polymers are made up of repeating monomer units which can be manipulated in various ways to give structures with desired properties.
- (a) Deduce the repeating unit of poly(2-methylpropene). (1)
- (b) Deduce the percentage atom economy for polymerization of 2-methylpropene. (1)
- (c) Suggest why incomplete combustion of plastics, such as polyvinyl chloride, is common in industrial and house fires. (1)
- (Total 3 marks)
10. (a) Predict the predominant type of bonding for a binary compound AB in which the electronegativity of both atoms is low. Use Section 17 of the data booklet. (1)
- (b) The type of bonding in a compound is sometimes used to classify materials. Outline why this type of classification has limitations by using magnesium diboride, MgB_2 , as an example. Refer to Sections 9 and 17 of the data booklet. (2)
- (Total 3 marks)

HL

11. A polyamide is broken down by hydrolysis. What are the two products formed?
- A a dicarboxylic acid and a diammonium salt
B an amine and a carboxylic acid
C a diamine and a dicarboxylic acid
D a dialcohol and an amine
12. A dipeptide forms by a condensation reaction between two amino acids. Which statement describes the reaction?
- A The reaction has an atom economy of 100%.
B The reaction forms an ester link and releases a molecule of water.
C The reaction involves the breaking of carbon-carbon double bonds.
D The reaction forms an amide link and releases a molecule of water.

HL end