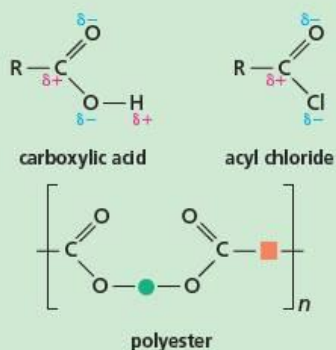


26 Carboxylic acids – derivatives and further reactions

Functional groups:



In this topic we look at the effect of structure on the acidity of carboxylic acids, and at further reactions of their derivatives.

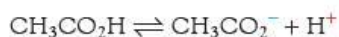
Learning outcomes

By the end of this topic you should be able to:

- 14.1a)** interpret and use the general, structural, displayed and skeletal formulae of the acyl chlorides
- 17.1a)** recall the chemistry of alcohols, exemplified by ethanol, in the formation of esters by acylation with acyl chlorides using ethyl ethanoate and phenyl benzoate as examples
- 19.1b)** describe the reactions of carboxylic acids in the formation of acyl chlorides
- 19.1c)** recognise that some carboxylic acids can be further oxidised: the oxidation of methanoic acid, HCO_2H , with Fehling's and Tollens' reagents, and the oxidation of ethanedioic acid, $\text{HO}_2\text{CCO}_2\text{H}$, with warm acidified manganate(VII)
- 19.1d)** explain the relative acidities of carboxylic acids, phenols and alcohols
- 19.1e)** use the concept of electronegativity to explain the acidities of chlorine-substituted ethanoic acids
- 19.2a)** describe the hydrolysis of acyl chlorides
- 19.2b)** describe the reactions of acyl chlorides with alcohols, phenols, ammonia and primary amines
- 19.2c)** explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides including the condensation (addition-elimination) mechanism for the hydrolysis of acyl chlorides.

26.1 The effect of structure on acid strength

As we saw in Topic 18, carboxylic acids are weak acids, and dissociate to a small extent when in aqueous solution:



They are more acidic than alcohols because the negative charge on the anion can be delocalised over two electronegative oxygen atoms. (see Figure 26.1).

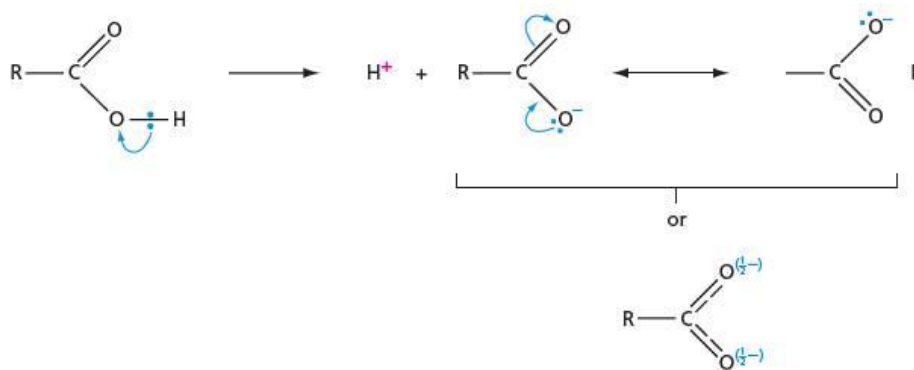
The increasing acidities of alcohols, phenols and carboxylic acids are explained by the increasing ability of the molecular structures to delocalise the negative charge in the alkoxide, phenoxide and carboxylate anions. Their relative acidities are demonstrated by their different reactions with sodium, sodium hydroxide and sodium carbonate (see Table 26.1).

Table 26.1 The use of Na, NaOH and Na₂CO₃ to illustrate the relative acidities of alcohols, phenol and carboxylic acids.

Reagent	Observation with		
	Hexanol	Phenol	Hexanoic acid
Na(s)	H ₂ (g) evolved	H ₂ (g) evolved	H ₂ (g) evolved
NaOH(aq)	no reaction	dissolves	dissolves
Na ₂ CO ₃ (aq)	no reaction	no reaction	CO ₂ (g) evolved

Atoms or groups that draw electrons away from the —CO₂[−] group will help the anion to form, and this causes the acid to be more dissociated (that is, to become a stronger acid). On the other hand, groups that donate electrons to the —CO₂[−] group will cause the acid to become weaker (see Table 26.2).

Figure 26.1 In the carboxylate anion, the charge is spread, increasing the stability of the ion.



Electron-donating groups decrease the acid strength of carboxylic acids, whereas electron-withdrawing groups increase their acid strength.

Table 26.2 The acidity of some carboxylic acids. Remember from Topic 22 that

$pK_a = -\log_{10} K_a$, where $K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$
for acids undergoing the dissociation
 $HA \rightleftharpoons H^+ + A^-$.

Formula of acid	pK_a	Percentage dissociation in 1.0 mol dm ^{−3} aqueous solution
	3.75	1.3%
	4.76	0.42%
	4.87	0.36%
	2.87	3.7%
	1.26	21%
	0.66	59%

Worked example

The pK_a of fluoroethanoic acid is 2.57.

- Does this mean it is a stronger or a weaker acid than chloroethanoic acid? Explain your answer.
- What pK_a would you expect for difluoroethanoic acid?

Now try this



- Use the data in Table 26.2 to predict the pK_a values of:
 - $(CH_3)_3C-CO_2H$
 - $Cl-CH_2-CH_2-CO_2H$
 Explain your reasoning.
- Explain why the pK_a values of 2-chlorobutanoic acid ($pK_a = 2.86$) and 4-chlorobutanoic acid ($pK_a = 4.53$) differ so much. Predict the pK_a value for 3-chlorobutanoic acid.

Table 26.3 The effect on pK_a for benzoic acid of electron-donating and electron-withdrawing groups

Answer

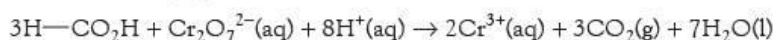
- The lower the pK_a , the larger is K_a . This means that the acid is more dissociated, and therefore stronger. Hence fluoroethanoic acid is a stronger acid than chloroethanoic acid. This is due to the greater electron-withdrawing ability of the highly electronegative fluorine atom.
- Difluoroethanoic acid would be expected to have a lower pK_a than dichloroethanoic acid – about 1.0.

The effect of electron-donating or electron-withdrawing groups is seen even when such groups are situated on the opposite side of a benzene ring to the $-CO_2H$ group (see Table 26.3).

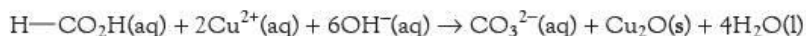
Formula of acid	pK_a	Percentage dissociation in 1.0 mol dm^{-3} aqueous solution
	4.20	0.80%
	4.37	0.73%
	3.99	1.0%

26.2 The further oxidation of some carboxylic acids

Unlike other aliphatic carboxylic acids, **methanoic acid** does not contain an alkyl chain attached to the $-CO_2H$ group. Instead, the $H-CO$ group, consisting of a hydrogen atom attached to a carbonyl group, has some reactions in common with aldehydes. In particular, it undergoes oxidation with common oxidants such as acidified dichromate(VI).



It also reacts with both Fehling's solution and Tollens' reagent (see page 301).



Ethanedioic acid contains two adjacent carbonyl groups. The proximity of two δ^+ carbon atoms weakens the $C-C$ bond sufficiently for the molecule to be readily oxidised by warm acidified manganate(VII).



This forms the basis of an accurate volumetric method of analysing solutions containing ethanedioic acid or its salts.

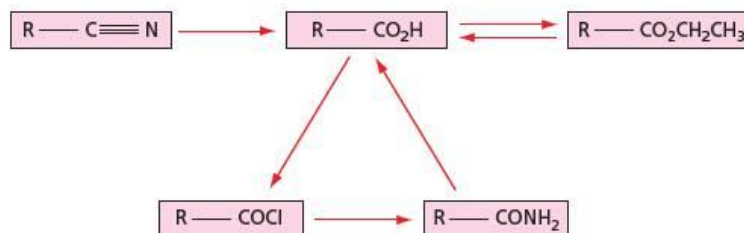
In a similar type of reaction, **α -ketoacids** are oxidised by alkaline H_2O_2 with the loss of a carbon atom.



26.3 Acyl chlorides

In section 18.3 we saw how acyl chlorides can be prepared from carboxylic acids. Most acid derivatives are prepared from carboxylic acids by the reactions described in this topic. Figure 26.2 shows a chart summarising the interrelationships between the various derivatives.

Figure 26.2 Interconversions between carboxylic acids and their derivatives



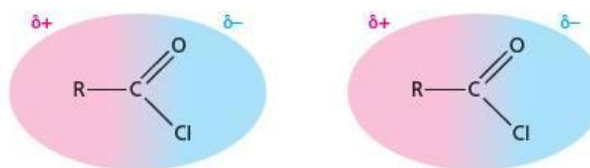
Now try this

Copy the chart in Figure 26.2 and write on each arrow the correct reagents and conditions for each reaction.

Properties of acyl chlorides

Acyl chlorides are usually liquids which fume in moist air. They are immiscible with water, but react slowly with it and eventually dissolve (see below). They are not hydrogen bonded: their main intermolecular attractions are a combination of van der Waals' forces and dipole–dipole forces (see Figure 26.3).

Figure 26.3 Dipole–dipole attractions in acyl chlorides



The extra electron-withdrawing effect of the carbonyl group, resulting in extra dipole–dipole attractions, has the effect of increasing the boiling point by about 10–15 °C compared with the boiling point of the halogenoalkane with similar shape (see Table 26.4).

Table 26.4 Strong dipole–dipole attractions increase the boiling points in acyl chlorides.

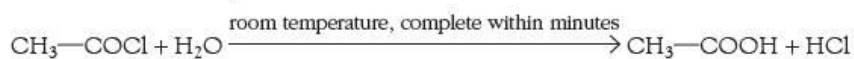
Chloroalkane	M_r	Boiling point / °C	Acyl chloride	M_r	Boiling point / °C	Difference / °C
	78.5	37		78.5	52	15
	92.5	68		92.5	80	12

Reactions of acyl chlorides

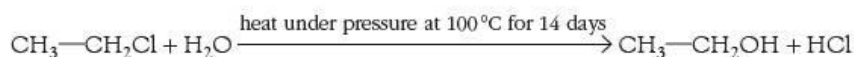
The electronegativity of the oxygen, and the easily polarised C=O double bond, have a dramatic effect on the reactivity of acyl chlorides compared with that of chloroalkanes.

With water

Acyl chlorides react readily with water:



Compare this with the conditions for the hydrolysis of a halogenoalkane:

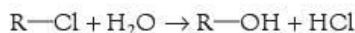


As a result of the speedy reaction with water acyl chlorides produce steamy fumes of HCl(g) when a few drops of water are added to them. This is a good test for them.

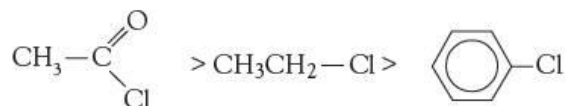
Now try this

Gather together all the information given in sections 15.3, 25.4 and this section to write an explanation of why the rates of hydrolysis of these three chloro compounds differ in this way. Would you expect the same relative rates with NH_3 or NaOH as the reagent, instead of H_2O ?

Together with what we have already seen in sections 15.3 and 25.4, we note that in the reaction:

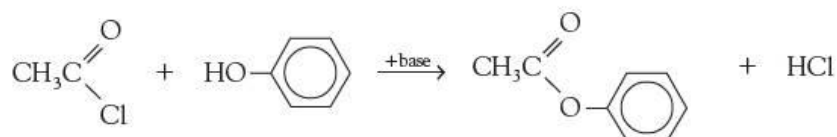
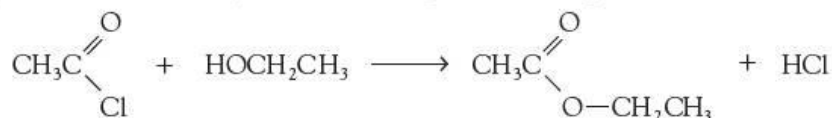


the relative rates of hydrolysis are as follows:

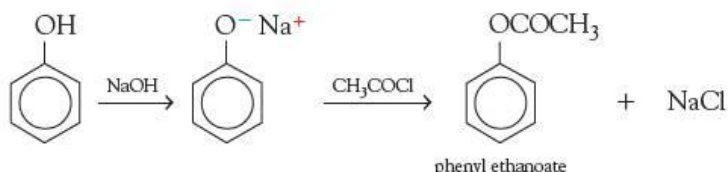


With alcohols or phenols

Acyl chlorides react readily with alcohols or phenols, forming esters:



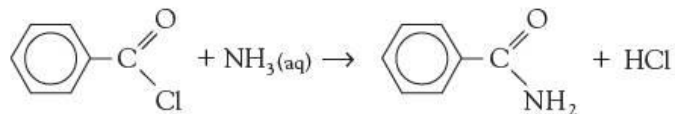
As mentioned in section 25.5, phenols are not so nucleophilic as alcohols, because the lone pair on the oxygen atom is delocalised over the ring. The acylation of phenols is therefore usually carried out under basic conditions (NaOH or pyridine have been used), when the more nucleophilic phenoxide ion is formed as an intermediate:



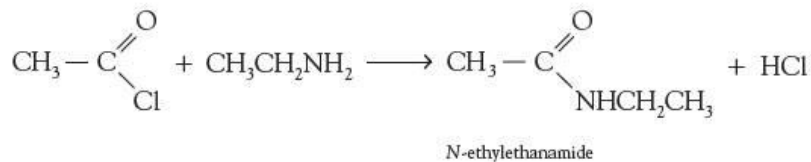
Because phenols do not react directly with carboxylic acids, this is the only method for preparing phenyl esters (see Topic 25, page 434).

With ammonia and amines

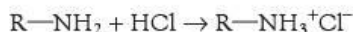
Acyl chlorides react with ammonia, forming amides. The reaction is vigorous, and white smoky fumes of $\text{NH}_4\text{Cl(s)}$ are often seen if an excess of ammonia is used.



They react with primary amines (see Topic 27), forming substituted amides:



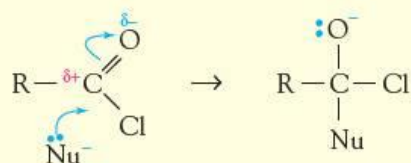
The hydrogen chloride produced reacts with another molecule of amine or ammonia in an acid–base reaction:



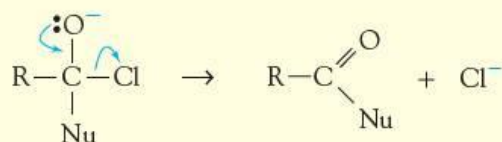
Therefore an excess of amine or ammonia is used to ensure complete reaction. The reactions of amides are described in section 27.5.

The mechanism of the reactions of acyl chlorides

The carbonyl group in acyl chlorides can undergo nucleophilic addition in a similar manner to carbonyl compounds:

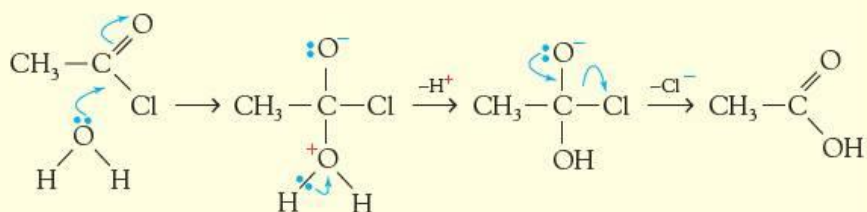


Unlike carbonyl compounds, however, acyl chlorides are provided with an easily removed leaving group, the chloride ion:



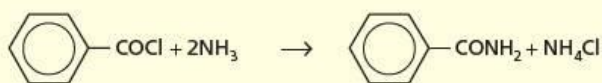
Nucleophilic substitution has taken place, by a mechanism involving addition, followed by elimination.

If the nucleophile is water, the carboxylic acid is formed:

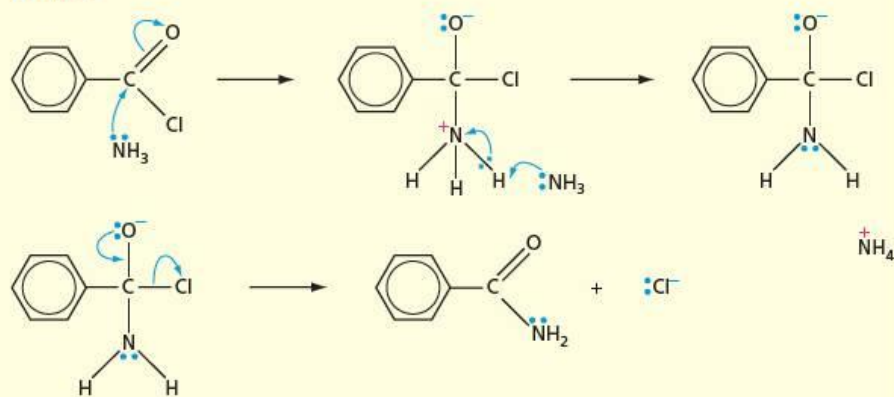


Worked example

Draw the mechanism for the reaction between ammonia and benzoyl chloride:



Answer



Now try this

Predict the products of, and suggest a mechanism for, the reaction between propan-1-ol and propanoyl chloride.

Explaining the relative reactivity of acyl chlorides, chloroalkanes and chloroarenes

As we saw in section 25.4, chlorobenzene does not undergo hydrolysis with water, or even with concentrated sodium hydroxide solution, due to the overlap of the lone pair on chlorine making the C—Cl bond stronger. Acyl chlorides, on the other hand, react much more readily than chloroalkanes with water or hydroxide. There are two reasons for this.

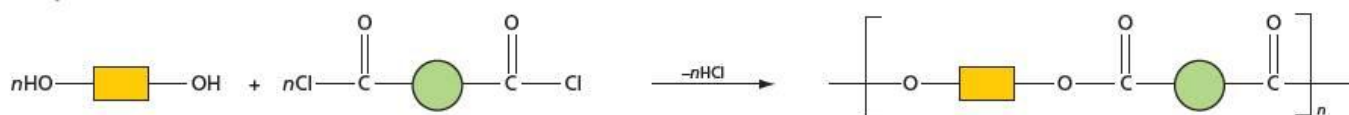
- 1 As we saw in the panel on page 445, the unsaturated nature of the C=O bond allows the C—OH bond to be formed before the C—Cl bond has broken. This **addition-elimination** mechanism therefore has a lower activation energy than the straight S_N2 reaction.
- 2 The carbon atom in acyl chlorides is attached to **two** electronegative atoms (oxygen and chlorine), and so is polarised δ^+ to a greater extent than the carbon atom in chloroalkanes. This allows it to attract nucleophiles more strongly.

26.4 Polyesters

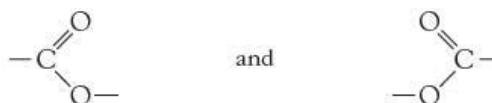
Formation of polyesters

When a diol is esterified with a diacid (for example, by heating with hydrogen chloride gas), or reacted with a diacyl chloride, a polyester is produced. Figure 26.4 shows the general reaction for esterification with a diacyl chloride. Here the yellow rectangles represent the rest of the diol molecule and the green circles represent the benzene ring in the diacyl chloride.

Figure 26.4 Formation of a polyester from a diacyl chloride



Notice that the direction of the ester bonds

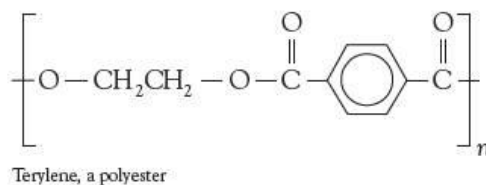
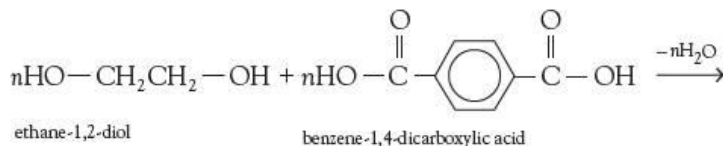


alternates along the chain.

Polyesters are examples of a class of polymers known as **condensation polymers**.

When monomers join together to form a **condensation polymer**, a small molecule such as H₂O, HCl or NH₃ is also produced.

The most commonly used polyester is Terylene, produced by polymerising ethane-1,2-diol and benzene 1,4-dicarboxylic acid, as shown below.



The polymer can be drawn into fine fibres and spun into yarn. Jointly woven with cotton or wool, it is a component of many everyday textiles. Material made from Terylene is hard-wearing and strong, but under strongly alkaline or acidic conditions the ester bonds can be hydrolysed, causing the fabric to break up.



Figure 26.5 Some products made from polyesters

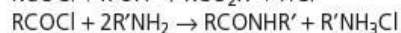
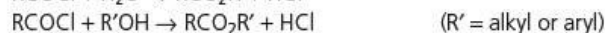
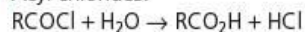
Further condensation polymers such as nylon and proteins are discussed in Topic 28.

Summary

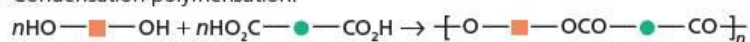
- The acid strength of **carboxylic acids**, RCO_2H , depends on their structures. In particular, electron-withdrawing chlorine atoms on the alkyl chain near to the CO_2H group increase its acid strength.
- Methanoic and ethanedioic acids can be oxidised further to CO_2 .
- **Acyl chlorides** are useful intermediates, forming **esters** with alcohols or phenols, and **amides** with amines.
- Acyl chlorides are much more easily hydrolysed than chloroalkanes.
- **Polyesters** are formed by the condensation of a diol with either a dicarboxylic acid or a diacyl chloride.

Key reactions you should know

- Acyl chlorides:



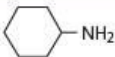
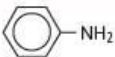
- Condensation polymerisation:



Examination practice questions

Please see the data section of the CD for any A_r values you may need.

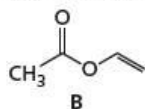
- 1 a Describe and explain how the acidities of $\text{CHCl}_2\text{CO}_2\text{H}$ and $\text{CH}_2\text{ClCO}_2\text{H}$ compare to each other, and to the acidity of ethanoic acid. [3]
- b For each of the following pairs of compounds, suggest one chemical test (reagents and conditions) that would distinguish between them. State the observations you would make with each compound, writing 'none' if appropriate.

first compound	second compound	test (reagents and conditions)	observation with first compound	observation with second compound
				
$\text{CH}_3\text{CH}_2\text{COCl}$	$\text{CH}_3\text{COCH}_2\text{Cl}$			
$\text{CH}_3\text{CH}_2\text{CHO}$	CH_3COCH_3			

[7]

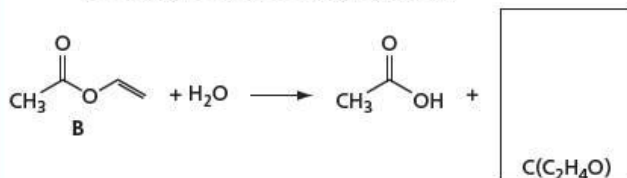
[Cambridge International AS & A Level Chemistry 9701, Paper 42 Q5 a & b June 2012]

- 2 a Polyvinyl acetate, PVA, is a useful adhesive for gluing together articles made from wood, paper or cardboard. The monomer of PVA is ethenyl ethanoate, B.



PVA is formed from B by the process of addition polymerisation.

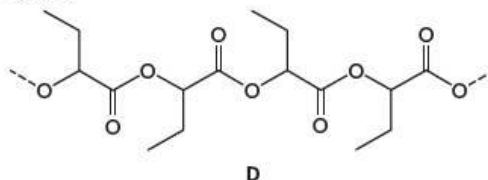
- i Draw a section of the PVA molecule containing at least 2 monomer molecules, and identify clearly the repeat unit.
- ii The ester B can be hydrolysed in the usual way, according to the following equation.



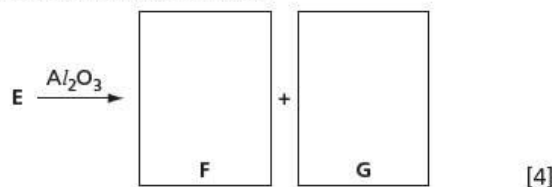
Use this information to suggest a possible structure for C and draw it

- iii When substance C is extracted from the product mixture, it is found that it **does** not decolourise $\text{Br}_2(\text{aq})$, but it does form a pale yellow precipitate with alkaline aqueous iodine. Suggest a structure for C that fits this new information.
- iv Suggest a confirmatory test for the functional group in the structure you have drawn in iii. Your answer should include the reagent you would use and the observation you would make. [6]

- b The following diagram represents a section of another polymer.



- i Copy and draw brackets, [], around the atoms that make up the repeat unit of this polymer.
- ii Name the functional group in polymer D.
- iii Suggest and draw the structure of the monomer, E, that could form this polymer.
- iv What type of polymerisation is involved in making polymer D from its monomer?
- v What is the relationship between the repeat unit of polymer D and the repeat unit of PVA? [5]
- c Monomer E exists as two stereoisomers. Heating either isomer with Al_2O_3 gives a mixture of two unsaturated carboxylic acids F and G, which are stereoisomers of each other.
- i Name the type of stereoisomerism shown by compound E.
- ii Suggest structures for F and G, and name the type of stereoisomerism they show.



[4]

[Cambridge International AS & A Level Chemistry 9701, Paper 42 Q4 June 2011]